

Natural Soil Colloids To Retard Simazine and 2,4-D Leaching in Soil

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Natural or synthetic sorbents for pesticides can be used to reduce contamination of soils and natural waters. The sorption of simazine and 2,4-D on montmorillonite minerals has been studied and their potential use to retard pesticide leaching in soil evaluated. Simazine and 2,4-D did not sorb on high-layer charge montmorillonite, whereas sorption on the lower layer charge montmorillonite SWy varied depending on the saturating cation. Simazine sorption increased in the order $\text{Ca}^{2+}\text{SWy} \ll \text{K}^{+}\text{SWy} < \text{Fe}^{3+}\text{SWy}$. Simazine molecules sorb on hydrophobic microsites of the montmorillonite. Once protonated, further sorption through cation exchange takes place in the interlamellar space of the montmorillonite, as corroborated by X-ray diffraction and FT-IR studies. 2,4-D does not sorb on K^{+}SWy or Ca^{2+}SWy , but does sorb on Fe^{3+}SWy , because the acidic character of this sorbent allows the molecular form of 2,4-D to sorb by hydrogen bonding and/or by hydrophobic interactions. Leaching experiments in hand-packed soil columns indicate that simazine and 2,4-D application as a complex with FeSWy renders later breakthrough and lower maximum concentration peaks, and the total herbicide leached is lower than when applied as the pure analytical grade compound. These results suggest the possible use of natural soil colloids as sorbents for herbicides such as simazine and 2,4-D to retard pesticide leaching in soil, thus reducing their ground water contamination potential.

Keywords: 2,4-D; leaching; montmorillonite; simazine; soil; sorption

INTRODUCTION

Agricultural and outdoor residential use of pesticides is a matter of environmental concern because these chemicals are recognized as a source of potential adverse environmental impact (nonpoint and point pollution) and their presence in surface and ground waters has grown considerably (Wauchope, 1978; Bouwer et al., 1988; Hallberg, 1989; Leistra and Boesten, 1989; Ritter et al., 1994; Templeton et al., 1998). Although herbicides have lower acute toxicity than insecticides, the presence of these chemicals in ground waters should be avoided because of their unknown long-term or cumulative effects (Leistra and Boesten, 1989; Cooper, 1993).

Soil-applied herbicides reach surface and ground waters by the losses associated with runoff and leaching processes (Beck et al., 1993). These losses are attenuated by the natural process of sorption by soil solids, mainly those constituting the soil colloidal fraction (Calvet, 1989). The greatest herbicide losses take place shortly after application, because molecules need time to diffuse into soil aggregates and reach sorption sites in soil colloids (Gish et al., 1991). If we favor or force sorption, these losses would be minimized. This is the principle of controlled-release (CR) formulations of herbicides (Gish et al., 1991; Mills and Thurman, 1994). Most CR formulations use natural or synthetic organic polymers (Johnson and Peperman, 1995; Hermosín et al., 1997) as herbicide carriers, although organoclays have recently been suggested as sorbents for CR formulations (Fernández-Pérez et al., 1998). Several authors have investigated the CR properties of clay minerals (Carr et al., 1994; Margulies et al., 1994; Johnson and Peperman, 1998).

The approach of our work is that natural soil components, such as mineral soil colloids, can be effective as herbicide sorbents to reduce their impact on surface and ground waters. Mineral soil colloids play an important role in sorption of polar organic compounds, mainly due to the high surface areas associated with their small particle size and, in the case of smectite clay minerals, because they have internal expandable surfaces accessible to polar organic molecules such as pesticides (Lagaly, 1994; Bailey and White, 1970; Hermosín et al., 1991, 1993; Cox et al., 1994, 1995, 1997; Pantani et al., 1997). Additionally, clay minerals as smectites are readily available and inexpensive materials.

The herbicides used in this study were simazine and 2,4-D, both widely used in agriculture. Simazine is relatively persistent and, despite its low water solubility (5 mg L^{-1}), its significance as a nonpoint source of contamination of water is recognized (Wauchope, 1978; Templeton et al., 1998; Agbekodo et al., 1996). 2,4-D is an anionic herbicide of relatively high water solubility (620 mg L^{-1}) and, as other anionic contaminants, its presence in ground water is a concern because anionic contaminants are weakly retained by most soil or sediment components (Fontaine et al., 1991; Hermosín and Cornejo, 1992). Celis et al. (1999), however, have recently shown that 2,4-D sorption by soil colloids can be very different depending on the interaction degree between the mineral and organic soil components. The objectives of this study were (i) to select a high-capacity natural sorbent for the herbicides simazine and 2,4-D, (ii) to test this sorbent's ability to retard simazine and 2,4-D leaching in soils and (iii) to assess the fundamental relationships between sorption mechanisms and leaching retardation. For this purpose, a column experiment with a sandy soil was conducted. Sandy soils subjected to high water inputs are considered to be a

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Table 1. Physicochemical Properties of the Sorbents Studied

| sorbent | pH ^a | CEC ^b (cmol _c /kg) | S _{BET} ^c (m ² g ⁻¹) | d ₀₀₁ (Å) | layer charge ^d (mol _c unit cell ⁻¹) |
|---------|-----------------|---|--|----------------------|--|
| CaSWy | 5.7/6.2 | 76 | 23 | 15.1 | 0.68 |
| FeSWy | 3.7/2.6 | 76 | 36 | 12.8 | 0.68 |
| KSWy | 6.3/6.3 | 76 | nd | 10.8 | 0.68 |
| CaSAz | 6.6/6.9 | 120 | 85 | 15.9 | 1.13 |

^a Determined in 1:500 and 1:100 w/v 0.01 M CaCl₂, respectively, after shaking for 24 h. ^b Van Olphen and Fripiat (1979). ^c Celis et al. (1998). ^d Total charge calculated from total chemical analysis (Jaynes and Boyd, 1991).

worst-case scenario for the appearance of pesticides in ground water (Cox et al., 1996).

MATERIALS AND METHODS

Herbicides. Simazine is a colorless solid of melting point = 226 °C, vapor pressure = 810 × 10⁻⁹ Pa (20 °C), and water solubility = 5 mg L⁻¹ (Worthing and Hance, 1991). The simazine used was the high-purity compound (>98%) purchased from Riedel-de Haën (Germany). 2,4-D is a colorless solid of melting point = 140.5 °C, vapor pressure = 53 Pa (160 °C), and water solubility = 620 mg L⁻¹ (Worthing and Hance, 1991). The 2,4-D used was the high-purity compound (>98%) purchased from Sigma (St. Louis, MO).

Soil and Montmorillonites. The soil used in the leaching and sorption experiments was a sandy-clay soil classified as Typic Rhodoxeralf. Soil texture (20% clay, 10% silt, and 70% sand) was determined by sedimentation and clay mineralogy (12% illite, 4% montmorillonite, and 4% kaolinite) by X-ray diffraction on oriented specimens (Jackson, 1975). Soil pH was 7.9 in a 1:2 (w/w) soil/deionized water mixture. The organic matter content (0.99%) was determined according to the Walkley-Black method (Jackson, 1975).

Wyoming (SWy) and Arizona (SAz) montmorillonites were supplied by The Clay Minerals Repository of The Clay Minerals Society. The <2 μm fraction of these clays was saturated with Ca²⁺ by five successive treatments with 1 M CaCl₂, washed with deionized water until Cl⁻ free, and freeze-dried. Fe- and K-saturated SWy montmorillonites were obtained by saturation of the <2 μm fraction (five treatments) with 1 M FeCl₃ or 1 M KCl. Some physicochemical properties of the sorbents studied are given in Table 1.

Sorption Experiments. Herbicide aqueous solutions in the micromolar range (*C*_{ini} = 2–10 μM) were shaken in 50 mL polypropylene centrifuge tubes with the soil (5 g of soil/10 mL of solution) or the different montmorillonites (0.05 g/25 mL of solution, in the case of simazine, and 0.1 g/10 mL in the case of 2,4-D) for 24 h at 20 ± 2 °C and centrifuged at 8000 rpm for 10 min. Previous studies confirmed no significant degradation of the chemical or sorption on the centrifuge tubes as well as attainment of equilibrium during this equilibration time. High soil/solution ratios in 2,4-D sorption studies were used due to the lack of sorption at lower ratios (0.05 g/25 mL of solution and 0.05 g/10 mL). Due to the high solubility of 2,4-D in water, 2,4-D sorption isotherms were also performed at higher initial solution concentrations (*C*_{ini} = 0.1–1 mM). Desorption (three cycles) was conducted at *C*_{ini} = 10 μM by replacing supernatant with distilled water. Suspensions were shaken for a further 24 h and centrifuged, and supernatants were analyzed. Equilibrium concentrations (*C*_e) were determined in supernatants by HPLC under the following conditions: 70:30 water/acetonitrile mixture for simazine and 55:45 diluted H₃PO₄ (pH = 2.0)/methanol for 2,4-D at 1 mL min⁻¹, Novapak C18 column (150 mm length × 3.9 mm i.d.), 25 μL injection volume, and UV detection at 230 nm. External calibration curves with standard solutions ranging from 2 to 10 μM and from 0.1 to 1 mM were used in the calculations.

X-ray Diffraction and FT-IR Spectroscopy Studies. FeSWy and KSWy (1 g) were treated with 2 mM (100 mL) aqueous solution of 2,4-D or 2 mM (100 mL) methanol solution of simazine. This high concentration of herbicide was used to

get an amount of herbicide sorbed on the clays sufficiently high to be analyzed by FT-IR and X-ray diffraction techniques. In the case of simazine, due to its low water solubility, methanol was used instead of water to obtain such a high herbicide concentration (2 mM). The clay–herbicide complexes and their corresponding blank samples (clays treated with methanol or water without herbicide) were heated at 110 °C and analyzed by X-ray diffraction with a Siemens D-5000 diffractometer (Siemens, Stuttgart, Germany) using Cu Kα radiation and by FT-IR spectroscopy with a Nicolet 5 PC spectrometer. X-ray diffractograms were obtained on oriented specimens and FT-IR spectra on KBr disks.

Synthesis of FeSWy–Simazine and FeSWy–2,4-D Complexes Used in Leaching Experiments. FeSWy (1 g) was treated with 100 mL of aqueous solution of 15 μM simazine or 1 mM 2,4-D, shaken for 24 h, and centrifuged. Supernatants were removed for analysis and, before air-drying, the solid was washed with distilled water. In this way the herbicide remaining in the FeSWy is sorbed to the clay. This procedure, in the case of simazine, was repeated four times because, due to its low water solubility, it was not possible to use high aqueous solution concentrations. The resulting clays with sorbed herbicide will be referred to as clay– or FeSWy–herbicide complexes.

Leaching Experiments. Leaching was studied in 30 × 5 cm methacrylate columns made up of six 5-cm-long sections sealed with silicon. The top ring was filled with sea sand and the bottom ring with sea sand plus glass wool, to minimize losses of soil and contamination of leachate with soil particles. The other four rings were hand-packed with 520 g of air-dried soil to give a bulk density of 1.32 g cm⁻³, saturated with 250 mL of 0.01 M CaCl₂, and allowed to drain for 24 h. Calculated pore volume of the columns after saturation was 40 ± 2%. The amounts of herbicide corresponding to an application rate of 1.5 (simazine) or 2.3 (2,4-D) kg ha⁻¹ were applied to the top of triplicate columns either as a methanol solution of the technical compound (5 mL of 60 mg simazine L⁻¹ or 5 mL of 90 mg 2,4-D L⁻¹ for free simazine and free 2,4-D) or as FeSWy complex with simazine or 2,4-D. The columns were leached with 0.01 M CaCl₂ at a rate of 50 mL day⁻¹ until no herbicide was detected by HPLC in the leachates. This was achieved within a 100-day period in the case of simazine and a 20-day period in the case of 2,4-D. After the leaching experiment, triplicate 5-g samples of soil from 0–5, 5–10, 10–15, and 15–20 cm depths in the column were extracted once with 10 mL of methanol by shaking for 24 h. The samples were centrifuged, and 2-mL aliquots were analyzed directly by HPLC for their herbicide content. Preliminary experiments showed that this extraction procedure recovered >95% of the herbicide applied to the soil.

RESULTS

Sorption–Desorption of Simazine on Soil and Montmorillonites. The simazine sorption–desorption isotherm on soil is plotted in Figure 1. Sorption is very low. The desorption branch, coinciding with the sorption one, indicates high reversibility of the process. Simazine did not sorb on SAz montmorillonite, which has a higher external surface area and layer charge than SWy montmorillonite (Table 1). Simazine sorption on diverse homoionic SWy samples increased in the order CaSWy << KSWy < FeSWy (Figure 2). Simazine sorption on Ca–SWy was highly reversible, whereas desorption isotherms showed hysteresis for FeSWy and KSWy montmorillonites. Although the method used for desorption analysis has been reported to be a source of sorption–desorption hysteresis (Bowman and Sans, 1985), the reversible sorption in the case of Ca–SWy indicates that irreversible sorption is the main source for the hysteresis effect observed in FeSWy and KSWy.

Sorption–Desorption of 2,4-D on Soil and Montmorillonites. 2,4-D did not sorb on soil, SAz, CaSWy,

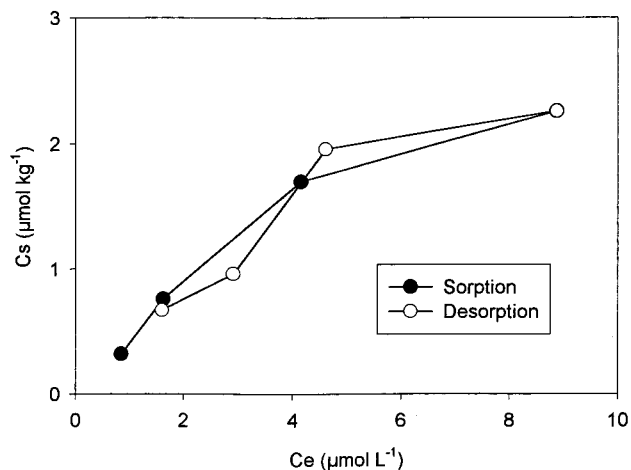


Figure 1. Simazine sorption–desorption isotherms on Typical Rhodoxeralf soil (1:2 soil/solution ratio). Error bars for the plotted points are smaller than symbols.

or KSWy. Sorption isotherms on FeSWy montmorillonite at two concentration ranges are shown in Figure 3, together with the desorption isotherm in the low

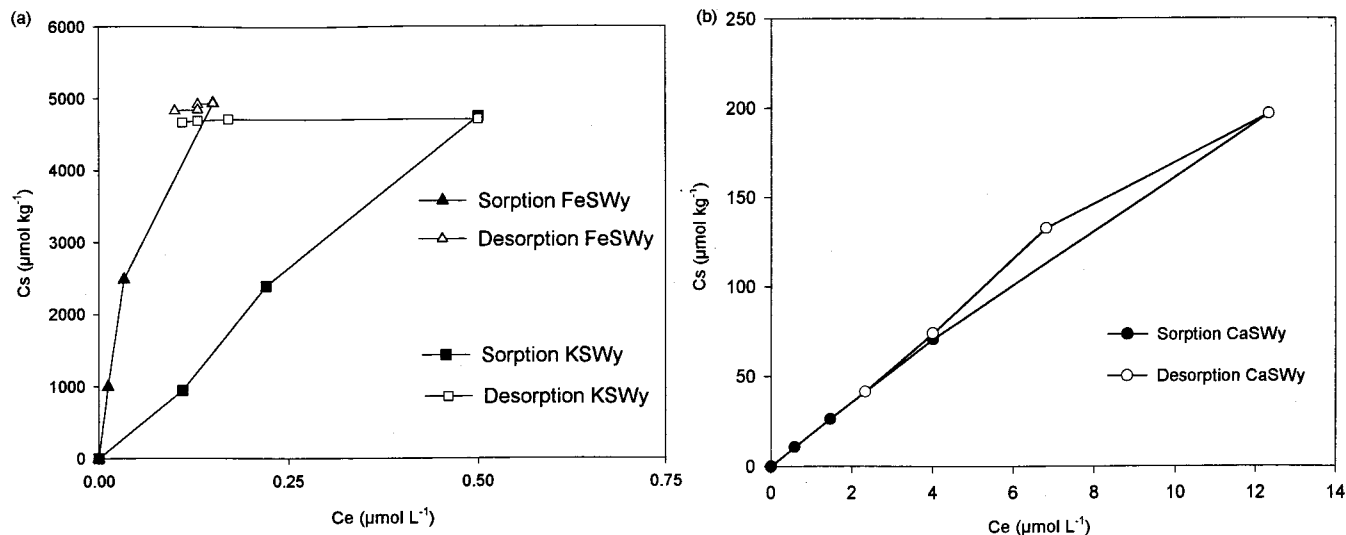


Figure 2. Simazine sorption–desorption isotherm on (a) FeSWy and KSWy and (b) CaSWy montmorillonites (1:500 solid/solution ratio). Error bars for the plotted points are smaller than symbols.

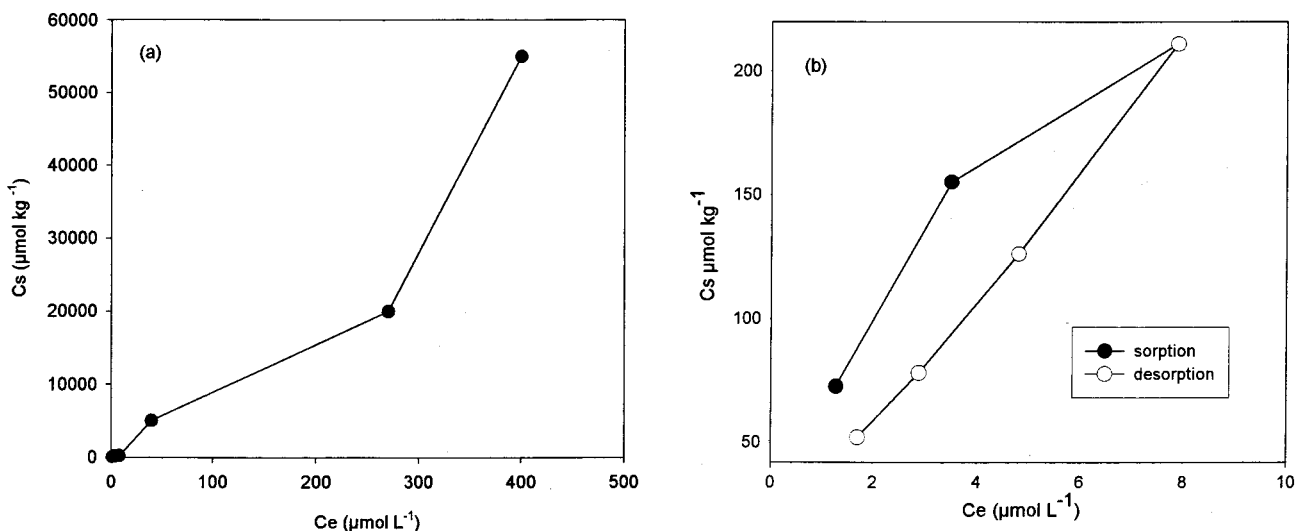


Figure 3. 2,4-D sorption–desorption isotherms on FeSWy montmorillonite (1:100 solid/solution ratio): (a) high concentration range; (b) low concentration range. Error bars for the plotted points are smaller than symbols.

concentration range. Sorption of 2,4-D on FeSWy is highly favored at high 2,4-D solution concentrations, indicating that sorption of 2,4-D molecules facilitates the sorption of further molecules. High-concentration solutions of 2,4-D yield lower pH (1 mM solution, pH 3) than low-concentration solutions (2 μ M solution, pH 6), which would contribute to increase the sorption of molecular 2,4-D species. Sorption is highly reversible, as shown by the desorption isotherm at low concentration range (Figure 3b), which is below the sorption isotherm.

X-ray Diffraction and IR Spectroscopy Studies.

X-ray diffraction analysis of the montmorillonite samples treated with a 2 mM methanol solution of simazine demonstrated that the interlamellar spacing of K–SWy remained unaffected upon sorption of 180 μ mol of simazine g^{-1} of clay, whereas the interlamellar spacing of FeSWy increased from 10.18 to 12.70 Å after sorption of 400 μ mol of simazine g^{-1} (Table 2). The basal spacing of FeSWy remained unaffected upon sorption of 100 μ mol of 2,4-D g^{-1} of clay after treatment with 2 mM aqueous solution of 2,4-D (Table 2).

FT-IR spectra of FeSWy–herbicide complexes and

Table 2. Basal Spacings (Å) of the Blank KSWy and FeSWy Samples (Methanol and Water Saturated) and Those of Simazine-Treated (2 mM Methanol Solution) or 2,4-D-Treated (2 mM Aqueous Solution) KSWy and FeSWy Heated for 24 h at 110 °C

| sample | untreated (MeOH) | untreated (H ₂ O) | simazine treated (MeOH) | 2,4-D treated (H ₂ O) |
|--------|------------------|------------------------------|-------------------------|----------------------------------|
| KSWy | 10.1 | | 10.3 (180) ^a | |
| FeSWy | 10.2 | 12.2 | 12.7 (400) | 12.1 (100) |

^a Numbers in parentheses are amounts of simazine or 2,4-D sorbed ($\mu\text{mol g}^{-1}$).

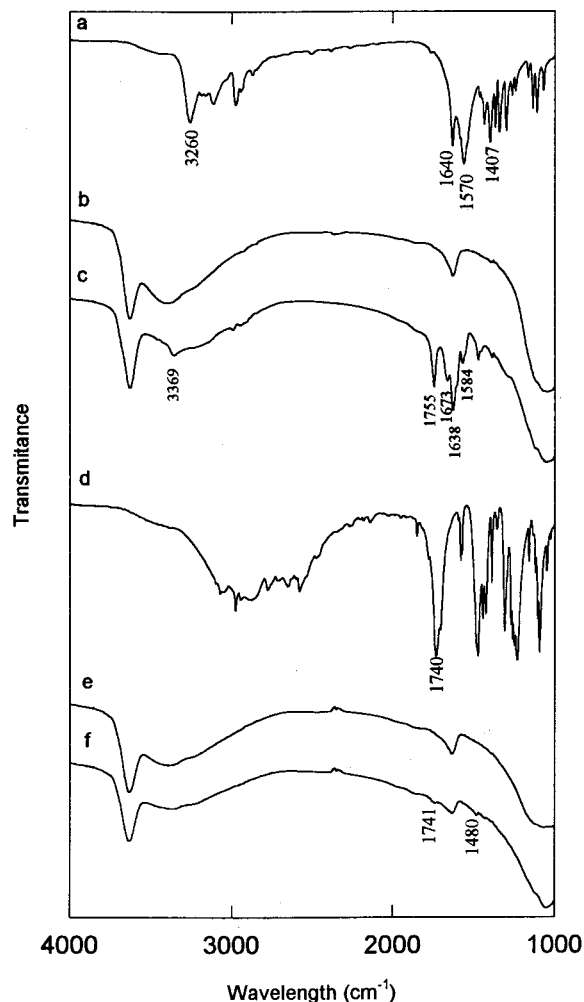


Figure 4. IR spectra of (a) simazine, (b) FeSWy montmorillonite saturated in methanol, (c) FeSWy-simazine complex ($400 \mu\text{mol g}^{-1}$ clay), (d) 2,4-D, (e) FeSWy montmorillonite saturated in water, and (f) FeSWy-2,4-D complex ($100 \mu\text{mol g}^{-1}$).

their corresponding blank clay samples together with those of pure simazine and 2,4-D are shown in Figure 4. Compared to the blank FeSWy sample, the FeSWy-simazine complex shows a great decrease in the 3420 cm^{-1} broad band corresponding to water associated with the interlayer cations of the clay (Figure 4b,c) (Hermosin et al., 1992; Cox et al., 1995). This decrease, although less pronounced, is also evident in the case of the FeSWy-2,4-D complex (Figure 4e,f).

The FT-IR spectrum of simazine (Figure 4a) undergoes significant changes as a result of interaction with FeSWy montmorillonite surface (Figure 4b,c). Absorption bands that, according to Bellamy (1975), correspond to NH stretching (3260 cm^{-1}) and to C=N stretching (1640 , 1570 , and 1407 cm^{-1}) are shifted to higher

frequencies (3369 , 1673 , 1638 , and 1584 cm^{-1} , respectively). However, the most significant feature is the appearance of a strong band at 1755 cm^{-1} , which corresponds to a carbonyl ($\nu_{\text{C=O}}$) band (Bellamy, 1975). According to Russell et al. (1968), this is due to protonation of a ring N followed by cleavage of the C-Cl bond and formation of the protonated hydroxy species as a result of interaction with the montmorillonite surface. This band is not present in the spectrum of the KSWy-simazine complex (data not shown), which shows only a weak band at 1638 cm^{-1} . In the case of 2,4-D (Figure 4d), there is a weak absorption band at 1741 cm^{-1} in the FeSWy-2,4-D complex (Figure 4e) that does not appear in the blank sample (Figure 4f), which has been assigned to C=O stretching of the undissociated 2,4-D species (COOH) (Celis et al., 1999).

Synthesis of the FeSWy-Simazine and -2,4-D Complexes Used in Leaching Experiments. Because IR results indicated that simazine acidic hydrolysis may occur when the clay-herbicide complex is prepared in methanol, the FeSWy-simazine complex to be tested in leaching experiments was prepared by successive saturation of the clay with a $15 \mu\text{M}$ aqueous simazine solution. After three successive sorption cycles, the amount of simazine sorbed on FeSWy was $5.5 \mu\text{mol g}^{-1}$ of clay. After a single sorption cycle with a highly concentrated aqueous solution (1 mM) of 2,4-D, the amount sorbed was $53.8 \mu\text{mol g}^{-1}$ of clay. Extraction of the complexes with methanol rendered recoveries $>95\%$ for simazine and $>98\%$ for 2,4-D.

Leaching in Hand-Packed Soil Columns. Simazine breakthrough (Figure 5a) occurs slightly earlier in the free simazine application than in the FeSWy-simazine application, and the maximum concentration peak appears slightly shifted to lower water volumes. This maximum concentration is reduced from $1.98 \mu\text{mol L}^{-1}$ in the free simazine system to $1.28 \mu\text{mol L}^{-1}$ in the FeSWy-simazine system. The total amount of simazine leached was slightly lower in the clay-simazine system (65%) than in the free simazine system (70%).

2,4-D breakthrough (Figure 5b) occurs earlier and leachate concentrations were higher than in the case of simazine, due to the higher application rate (2.3 versus 1.5 kg ha^{-1}) and the lack of sorption of 2,4-D on soil. The maximum of the breakthrough curve (BTC) is slightly shifted to the right in the case of the clay-associated 2,4-D system and, as in the case of simazine, the maximum concentration peak is lower when 2,4-D is applied as a complex with FeSWy ($16.8 \mu\text{mol L}^{-1}$) than when free 2,4-D is applied ($20.5 \mu\text{mol L}^{-1}$). The total amounts accumulated in leachates were lower for the clay-2,4-D complex (70%) than for the free 2,4-D (80%).

After leaching, the soils were extracted with methanol and no significant amounts of simazine or 2,4-D were detected in either system (free or complexed herbicide application). In the case of the free technical compound, the difference between the amount of pesticide applied and the amount recovered is attributed to soil-bound or degraded herbicide. Both processes are favored in column experiments compared to batch experiments (Cox et al., 1996). In the case of the clay-herbicide complexes, the soil-bound or degraded herbicide should be nearly the same; thus, the 5–10% increase in nonextractable herbicide could correspond to irreversibly sorbed herbicide in the clay complex. Extraction of the clay-herbicide complexes with methanol rendered

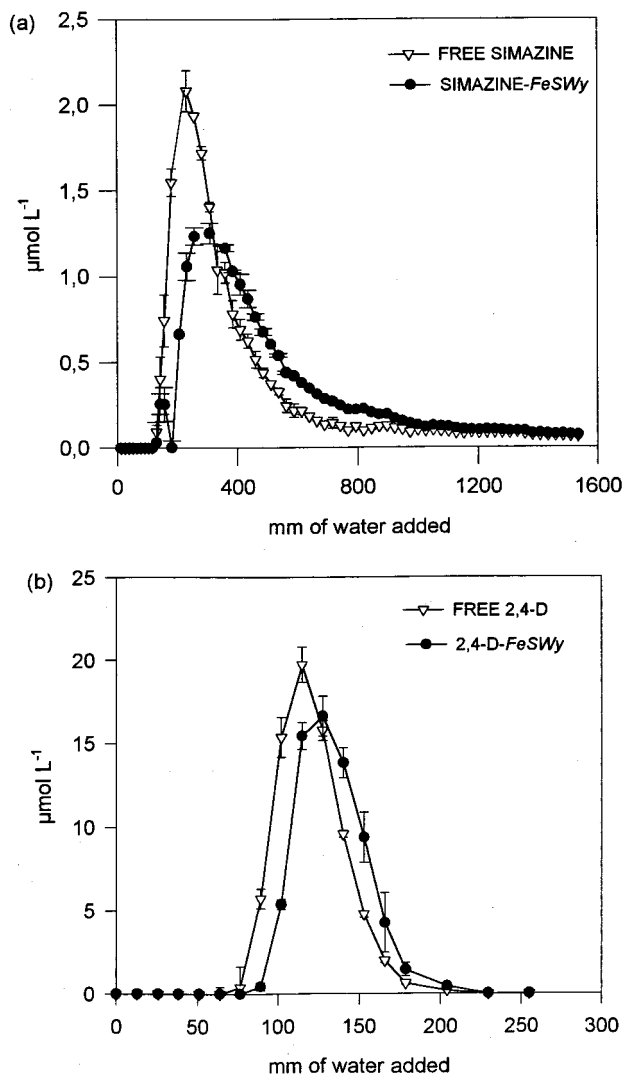


Figure 5. (a) Simazine BTCs in control columns (free simazine) and in columns to which simazine was applied as a complex with FeSWy; (b) 2,4-D BTCs in control columns (free 2,4-D) and in columns to which 2,4-D was applied as a complex with FeSWy.

recoveries of 95% for simazine and 98% for 2,4-D of the amounts calculated to be sorbed.

DISCUSSION

The low sorption of simazine and the lack of sorption of 2,4-D on the soil studied agree with the low soil content in smectitic clay and organic matter, which are the soil components related to sorption of these two herbicides (Hayes, 1970; Grover and Smith, 1974; Moreale and Van Bladel, 1980; Laird et al., 1994; Celis et al., 1997, 1998, 1999). Also, the high pH of the soil (7.9) would negatively contribute to sorption of anionic compounds such as 2,4-D, due to the repulsions between 2,4-D anions and negatively charged soil surfaces. FeSWy montmorillonite is, among all sorbents studied, the best sorbent for simazine and 2,4-D.

The lack of sorption of simazine on CaSAz and the measured sorption on CaSWy suggest that simazine sorption takes place on hydrophobic microsites located between the charge sites on montmorillonite surfaces, more abundant in SWy than in SAz due to the lower surface charge density of SWy (Laird, 1996; Celis et al., 1997). This is confirmed by the very high sorption

measured in the low hydrated K^+ -saturated montmorillonite KSWy, because the low hydration of potassium ions allows more hydrophobic spaces than strongly hydrated cations such as Ca^{2+} (Haderlein et al., 1996). If an acidic medium is provided, as in the case of FeSWy (Table 1), protonation and sorption by cationic exchange of simazine can further occur. Celis et al. (1997) have observed this phenomenon at pH up to 2 units above the pK_a of simazine. According to Celis et al. (1997), sorption of *s*-triazines as protonated species on montmorillonites must be preceded by sorption as molecular species on hydrophobic microsites of the clay unless the pH of the bulk solution is close to the pK_a . The pH of the clay surface is as much as 2–3 units lower than that of the bulk solution (Mortland, 1970) and the higher polarizing cation of the montmorillonite increases both the strength and the number of acid sites (Frenkel, 1974). Taking into account that at the solid/solution ratio used in sorption experiments (1:500) the pH of the bulk solution ranged from 4 to 5 and that simazine $pK_a = 1.7$, this herbicide would initially sorb on hydrophobic sites in molecular form. Surface acidity of the clay would further allow protonation to occur, and sorption by cation exchange proceeds. The contribution of cationic exchange to simazine sorption on FeSWy would explain the higher sorption on FeSWy when compared with CaSWy and KSWy montmorillonites. The decrease in interlamellar water observed by FT-IR (Figure 4) supports some substitution of Fe^{3+} ions with their hydration water by protonated simazine. This cationic exchange sorption reaches only 10% of the CEC of SWy in water, whereas in methanol it is enhanced up to 55% of the CEC of SWy. In an alcoholic medium such as methanol, the high polarization of the remaining water molecules at the clay surface promotes protonation of the sorbed simazine molecules, which in turn facilitates the chemical hydrolysis of simazine to hydroxysimazine (Russell et al., 1968). The increase in the basal spacing of FeSWy upon saturation with a methanol solution of simazine (Table 2) suggests sorption takes place primarily in the interlamellar space of the montmorillonite. The lack of sorption of simazine on SAz–montmorillonite also suggests interlamellar sorption in SWy, because lower layer charge (SWy) facilitates the opening of the silicate layer and thereby interlamellar sorption (Cox et al., 1994, 1995, 1997; Pantani et al., 1997). In the case of KSWy, the high irreversibility of simazine sorption suggests interlamellar sorption, although the relatively low amounts of simazine sorbed ($180 \mu\text{mol g}^{-1}$) compared to the CEC of the clay ($760 \mu\text{mol}_{\text{charge}} \text{g}^{-1}$) and the flat position of the sorbed molecules (Weber, 1970) would render a basal spacing similar to that of the original montmorillonite (Table 2).

2,4-D ($pK_a = 2.6$) sorbs only on FeSWy montmorillonite and not on soil or other montmorillonites studied, because the acidic medium favors the association of anionic species with hydrogen ions, forming neutral molecules and allowing weak physical interactions and hydrogen bonding (through the carbonyl group of the molecule and clay surface water molecules) and hydrophobic interactions to take place. This is confirmed by the $C=O$ absorption band of the molecular species observed in the IR spectrum of the FeSWy–2,4-D complex. These interactions are not possible at higher pH due to the repulsion between negatively charged clay surface and 2,4-D anions. The low pH of the bulk solution would also allow interaction between molecular

species of 2,4-D at the sorbent surface, because the sorption isotherm does not reach the saturation plateau, increasing sorption exponentially with the amount of 2,4-D sorbed (Figure 3). However, all of those 2,4-D/FeSWy interactions are weak, as suggested by the highly reversible sorption of 2,4-D on FeSWy. The 2,4-D desorption isotherm (Figure 3) is below the sorption isotherm because of an increase in pH during desorption cycles (up to pH >5). The lack of sorption of 2,4-D at lower solid/solution ratio is also attributed to the increase in pH of the bulk solution (Table 1). The fact that the basal spacing of FeSWy remained unaffected upon sorption of 100 μmol of 2,4-D g^{-1} and the high reversibility of sorption (Figure 3) suggest that 2,4-D molecules sorb primarily at easily accessible external surfaces or outer interlamellar spaces.

The low, reversible sorption of simazine on the soil studied and the lack of sorption of 2,4-D on the soil suggest high leaching potential of both herbicides. When simazine and 2,4-D are applied as complexes with FeSWy, the maximum concentration peaks were lower than when those corresponding to free simazine or 2,4-D were applied, due to sorption on FeSWy (Figure 5). The shift of this maximum to higher water volumes has also been attributed to sorption processes (Garmendier et al., 1993) and here is confirmed. The longer tailing of the BTC in the case of simazine applied as a complex is produced by the hysteresis observed in the desorption experiments (Brusseau and Rao, 1989; Garmendier et al., 1993), which extends the presence of simazine in soil solution at low concentrations. The association of both herbicides with Fe^{3+} SWy decreases both the herbicide concentration in the leachates and, to a lesser extent, the total herbicide loss in the leachates from the sandy soil.

Environmental Implications. Sorption experiments show that the low charge SWy montmorillonite saturated with Fe^{3+} is a very effective natural soil colloid for simazine and 2,4-D sorption. Sorption is highly irreversible in the case of simazine due to sorption by cationic exchange and highly reversible in the case of 2,4-D due to sorption as molecular species by weak physical interactions. The results of the leaching experiment show that the association of both herbicides with ferric low charge montmorillonite could effectively decrease and delay the leaching losses of simazine and 2,4-D, thus reducing the contamination of ground water by soil-applied simazine and, to a lesser extent, 2,4-D. The results of the present work suggest the possible use of FeSWy as a support to design formulations of simazine and 2,4-D. Those formulations would require a herbicide content higher than that of the complexes used in this work and should be checked for weed control before they can be used in the field.

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