Adsorption and Desorption of Imazosulfuron by Soil

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Understanding and quantifying the adsorption and desorption of herbicides by soil is important for predicting their fate and transport in the environment. Here we report a study concerning the adsorption and desorption, by four different soils, of imazosulfuron, 1-(2-chloroimidazo[1,2-*a*]pyridin-3-ylsulfonyl)-3-(4,6-dimethoxypyrimidin-2-yl)urea, a new sulfonylurea herbicide. Both phenomena are well-described by the Freundlich equation, which shows this herbicide to be little adsorbed by each of the four soils investigated. The Freundlich adsorption constants, K_{f-ads} , ranged from 1.46 to 3.02. Distribution coefficients between soil and water, K_d , measured on soils of different organic matter contents and pH values showed an important effect of these two parameters on imazosulfuron retention. The Freundlich desorption data indicated that a significant amount of the imazosulfuron sorbed is not easily desorbed. The desorption process showed an evident hysteresis phenomenon, which may contribute to the persistence of imazosulfuron in soil.

Keywords: Imazosulfuron; sulfonylurea herbicide; adsorption; desorption

INTRODUCTION

The fate and mobility of herbicides in the environment are important in predicting their leaching potential through soil and their movement to and dispersion in aquatic sites (Bailey and White, 1970; Hance 1980). Adsorption is an important process for determining the ultimate fate of organic chemicals in soils because detoxification mechanisms, such as degradation, metabolism, microbial uptake, and mobilization, are operative only on the nonsorbed fraction of molecules (Weber and Miller, 1989; Pignatello and Xing, 1996; Sims et al., 1991). The extent of adsorption is related to various soil properties, including organic matter content, type and amount of clay, ion exchange capacity, and pH. Moreover, various physicochemical parameters of the compound, such as water solubility and octanol-water partition coefficient, also play an important role in determining the extent of adsorption (Singh et al., 1990; Barriuso et al., 1992).

Sulfonylurea herbicides are used to control broadleaved weeds and some grasses in cereal crops. They are selective systemic herbicides absorbed by the foliage and roots and rapidly translocated to the meristematic tissues. These herbicides act by inhibiting cell division and have relatively low acute mammalian toxicity (Hay, 1990). The environmental fate of several sulfonylureas has been reported (Harvey et al., 1985; Schneiders et al., 1993; Vicari et al., 1996). Imazosulfuron, 1-(2chloroimidazo [1,2-*a*]pyridin-3-ylsulfonyl)-3-(4,6-dimethoxypyrimidin-2-yl)urea (Figure 1), is a relatively new sulfonylurea herbicide, and no information is available in the literature about its mobility in soils under either laboratory or field conditions.

The objective of this study was to determine the adsorption and desorption characteristics of imazosul-



Figure 1. Chemical structure and main physicochemical properties of imazosulfuron (data from *Pesticide Manual* (Tomlin, 1994)).

furon on four Italian soils as a preliminary step for modeling purposes. Data regarding adsorption and desorption are needed to formulate suitable models to estimate persistence and mobility under different conditions of utilization.

MATERIALS AND METHODS

Chemicals. Imazosulfuron (Figure 1), and its metabolites, IPSN (2-chloroimidazo[1,2-a]pyridin-3-sulfonamide) and HMS (1-(2-chloroimidazo[1,2-*a*]pyridin-3-ylsulfonyl)-3-(4-hydroxy-6-methoxypyrimidin-2-yl)-urea), were provided by Takeda Chemical Industries, Ltd. The third metabolite, ADPM (2-amino-4,6-dimethoxypyrimidine), was bought from Sigma-Aldrich (Milan, Italy) and had a purity of 98%. All were used without further purification. All solvents used were pure analytical HPLC grade solvents (Carlo Erba, Milan, Italy).

Soils. Four Italian soils with different physical and chemical properties were selected for this study. Fresh soils from a 0-15 cm depth were collected, air-dried, and ground to pass a 2 mm sieve prior to use. The physicochemical characteristics of the soils are given in Table 1. They have been classified according to the soil classification scheme given in Agricultural Handbook 436 (1975).

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Table 1. Selected Physical and Chemical Properties of the Soils Investigated

		-		-		
soils	total sand (%)	silt (%)	clay (%)	OC (%)a	$\mathbf{p}\mathbf{H}^{b}$	CEC ^c (meq/100 g)
sandy loam no. 1	60.03	25.92	14.05	1.40	7.0 ± 0.1	10.6
sandy loam no. 2	62.20	28.40	9.40	0.60	4.5 ± 0.1	11.4
sandy clay loam no. 3	61.50	5.35	33.15	3.80	7.4 ± 0.1	31.8
sandy clay no. 4	46.36	12.91	40.73	1.70	7.5 ± 0.1	30.2

^a Organic carbon content. ^b Measured in 1:2.5 (w/w) soil/KCl aqueous solution (1 M). ^c Cation exchange capacity.



Figure 2. Adsorption kinetics of imazosulfuron at 25 ± 2 °C.

Adsorption Experiments. The adsorption of imazosulfuron was determined using the batch equilibrium method (OECD, 1981). Triplicate samples of 1 g (dry weight) of soil were equilibrated in centrifuge tubes with 25 mL of herbicide solution at 25 \pm 2 °C. Three standard solutions containing imazosulfuron in acetonitrile at different concentrations were prepared. The herbicide working solutions were obtained by diluting a 1 mL aliquot of each standard to 100 mL with aqueous 0.01 N CaCl₂ at final concentrations of 4.6, 8.5, and 17.8 μ g/mL. Calcium chloride was used to keep the ionic strength of the soil solution constant and to facilitate flocculation. Due to the slow dissolution rate of imazosulfuron in aqueous 0.01 N CaCl₂, the addition of acetonitrile was useful in achieving its complete dissolution within a reasonable time. The tubes were placed on a reciprocating shaker for 20 h.

The period of time was selected through preliminary kinetic studies carried out by adding 25 mL of a 5 μ g/mL imazosulfuron solution to 1 g of soil. At different intervals of time (2, 4, 6, 8, and 24 h), the samples were removed and centrifuged at 5000 rpm and the supernatant was analyzed as described below. Equilibrium was reached within 2 h; further decreases in the imazosulfuron concentration in the supernatant until after 24 h were not significant (Figure 2), with 20 h taken as the equilibration time for laboratory convenience.

Quantification of herbicide amounts sorbed by the various soils tested was performed as follows. After equilibration, the suspensions were centrifuged at 5000 rpm for 15 min and 5 mL of the supernatant was filtered and analyzed immediately. The amount sorbed by the soil was calculated from the difference between the initial and the final concentration of imazosulfuron in solution. Additionally, blanks with the initial solutions of imazosulfuron at concentrations of 4.6, 8.5, and 17.8 μ g/mL without soil were prepared: the control samples analyzed did not show any adsorption of the herbicide onto the glass of the tube nor significant losses due to volatilization and hydrolysis.

The effect of pH on imazosulfuron adsorption by soil was examined by applying the batch equilibrium method to pH-modified soils. The pH of the four soils investigated was modified by adding 30 mL of HCl solution (0.2, 0.5, 1.0, and 2.0 N) to 10 g of soil (without herbicide) and then equilibrating

for 2 h at 25 ± 2 °C. After treatment, pH values of the soils treated were measured potentiometrically in 1:2.5 (w/w) soil/1 M KCl aqueous solution (SISS, 1985a).

Blanks were prepared by adding 25 mL of aqueous 0.01 N $CaCl_2$ with 1% of acetonitrile (v/v) to 1 g of each soil or pH-modified soil. The tubes were placed on a reciprocating shaker for 20 h. The pH value of the supernatant measured before and after shaking did not vary significantly.

Adsorption was also studied in sandy clay soil no. 4 with reduced organic matter content achieved by treatment with H_2O_2 , according to the procedure proposed by Lavkulich and Wiens (1970). A 15 g amount of soil was added to 75 mL of 35% H_2O_2 (v/v) and diluted 1:2 with water. The suspension was stirred at room temperature until frothing had completely subsided (~24 h). The samples were then centrifuged and dried for 2 h at 40 \pm 2 °C. The soils treated were analyzed for residual organic matter content by the dichromate oxidation method (SISS, 1985b).

The organic solvent level in the imazosulfuron solution might influence adsorption on the soil. Another part of this study concerned the evaluation of the possible influence of acetonitrile on adsorption. Adsorption was studied by applying the batch equilibrium method to sandy clay loam soil no. 3 with solutions containing different levels of acetonitrile in water. A stock solution of imazosulfuron in acetonitrile was prepared. Aliquots of the stock solution were appropriately diluted with aqueous 0.01 N CaCl₂ to obtain imazosulfuron work solutions at a concentration of 4.8 μ g/mL with different percentages of acetonitrile, spanning over a range of 0.8–4.0%.

Desorption Experiments. After the adsorption process described above, 5 mL of the supernatant withdrawn was compensated for sampling by adding 5 mL of aqueous 0.01 N CaCl₂ with 1% acetonitrile (v/v). The tubes were placed on a reciprocating shaker for 24 h at 25 ± 2 °C. Preliminary kinetic studies showed that desorption reached equilibrium within 24 h. After shaking, the suspensions were centrifuged, and 5 mL of supernatant withdrawing and replacing, and reequilibrating) were repeated four times.

Imazosulfuron Analysis. Herbicide concentrations were determined by high-performance liquid chromatography (HPLC) by a HPLC system (Model 600 pump, 486 UV detector operating at 238 nm; Waters, Milford, MA) and a computing integrator chromatography workstation (Model PU 4810; Philips, U.S.A.), equipped with a Prodigy C-18 reversed phase column (250 \times 4.6 mm, particle size 5 μm) from Phenomenex (Torrance, CA). The mobile phase was a 60/40 (v/v) mixture of acetonitrile/0.1% (v/v) aqueous acetic acid (pH 3.5). The flow rate was 1.0 mL/min. Under these conditions the retention time of imazosulfuron was 6.8 min, whereas for its metabolites it was 3.3 min for ADPM, 3.0 min for IPSN, and 2.7 min for HMS. Blanks were prepared by adding 25 mL of aqueous 0.01 N CaCl₂ with 1% of acetonitrile (v/v) without herbicide to 1 g of soil and treated as described above (see Adsorption Experiments). They did not exhibit any peak that interfered with herbicide and/or its metabolites detection.

Herbicide standard solutions were prepared in acetonitrile and stored at 4 °C in the dark until use. Two calibration curves were obtained by injecting 20 μ L samples of solutions at 0.025, 0.050, 0.250, 0.500, 1.000, 1.500 μ g/mL and 2.10, 5.25, 10.50, 21.00 μ g/mL, respectively. A linear relationship between chromatographic peak areas and amounts of imazosulfuron was found over these concentration ranges, and $r^2 = 0.9998$ was obtained in each case. The detection limit (LOD) (estimated to be three times the background noise) was 50 ppb (μ g/L). The limit of quantitation (QOD) (estimated to be 10 times the background noise) was 165 ppb (μ g/L). No significant difference in background noise was observed between the analyses of the standards in acetonitrile and those of the matrix analyzed. Therefore the QOD limit for the analyses on matrices can be assumed to be the same as that observed for standards.

To validate daily the performance of the analytical method, the imazosulfuron solutions (99:1 (v/v) 0.01 N aqueous CaCl₂/ acetonitrile) used to perform adsorption–desorption experiments on soils were analyzed by HPLC. Peak areas were compared with those of pure analytical standards in acetonitrile. The recoveries were always greater than 99%. Replicate analyses of standards at 4 day intervals gave good reproducibility (RSD < 3%), which ensured the repeatability of the analytical method. Moreover standard solutions were prepared weekly to avoid degradation.

Data Analysis. The amount of imazosulfuron sorbed after equilibration was calculated from the difference between initial and equilibrium solution concentrations. Adsorption and desorption data were fitted to the linearized form of the Freundlich equation

$$\log C_{\rm s} = \log K_{\rm f} + 1/n_{\rm f} \log C_{\rm e} \tag{1}$$

where $C_{\rm s}$ is the herbicide etquilibrium concentration in the soil after adsorption–desorption ($\mu g/g$), $C_{\rm e}$ the equilibrium concentration in solution ($\mu g/mL$), and $K_{\rm f}$ and $n_{\rm f}$ are the constants characterizing the adsorption–desorption capacity and intensity, respectively.

The distribution coefficient, K_d , was calculated for the lowest initial concentration as follows:

$$K_{\rm d} = C_{\rm s}/C_{\rm e} \tag{2}$$

This was normalized to the organic carbon content of the soil investigated (OC) by calculating K_{oc} according to the equation

$$K_{\rm oc} = K_{\rm d} \times 100\% \rm OC \tag{3}$$

Hysteresis coefficients, *H*, were calculated for the adsorption–desorption isotherms as follows:

$$H = (1/n_{\rm f-ads})/(1/n_{\rm f-des})$$
 (4)

where $1/n_{f-ads}$ and $1/n_{f-des}$ are the Freundlich constants obtained for the adsorption and desorption isotherms, respectively.

RESULTS AND DISCUSSION

The adsorption isotherms obtained for each of the soils investigated varied in shape according to the characteristics of the soil (Figure 3). The isotherm of the sample with higher OC and clay contents (soil no. 3) resembles the C-type isotherm described by Giles et al. (1960). The C-type isotherm is characterized by a slope that is independent of solution concentration and produced by a constant partitioning between the adsorbent and the solution phase. As we expected, the highest adsorption was observed for soil no. 3. In fact, the simultaneous occurrence of high OC and clay content in soil no. 3, as compared to the other soils, supports the hypothesis that it is the soil with the highest number of adsorption sites. Only the isotherm of soil no. 2, with low clay and organic matter contents, resembles the S-type isotherm. This isotherm type indicates a low imazosulfuron-soil affinity at low concentrations, with strong competition with the aqueous phase. Adsorption becomes easier as the concentration of imazosulfuron in the aqueous phase increases (Calvet, 1989).



Figure 3. Adsorption isotherms of imazosulfuron on the soils investigated.

The adsorption of imazosulfuron may be described in all cases by the linearized form of the Freundlich equation (eq 1; $r^2 \ge 0.95$). The constants $K_{\text{f-ads}}$ and 1/n, together with the correlation coefficients (r^2) for the linear fits, are given in Table 2. The distribution coefficient, K_d (eq 2), and the distribution coefficient normalized for the organic carbon content, K_{oc} (Eq 3), were also calculated for the lowest initial concentration. The values of K_{f-ads} and K_d (Table 2) were used in the present work to compare the adsorption of imazosulfuron by the different types of soil. Imazosulfuron yielded very low K_{f-ads} and K_d values, as expected considering its low octanol-water partition coefficient and moderate solubility in water (see values reported in Figure 1) (Briggs, 1981). Moreover the K_{f-ads} and K_d values calculated were in agreement with those reported for most sulfonylureas (Harvey et al., 1985; Walker and Welch, 1989; Schneiders et al., 1993; Vicari et al., 1996). However, higher values for these constants were observed for soils with higher clay or organic matter content. As a matter of fact, organic matter content, pH, and clay are known to play a major role in the adsorption of sulfonylureas.

To determine by statistical approximation the degree of influence of each soil characteristic on adsorption, simple regression analyses between K_{f-ads} or K_d and the chemical and textural characteristics of the soil-such as organic matter content (OC), pH, clay, and cation exchange capacity (CEC)-were performed. A significant positive relationship was found between K_d and OC (r^2 = 0.97), which improved when the K_d value of soil no. 2, characterized by a quite different pH value (pH =4.5), was excluded $(r^2 = 0.99)$. No significant relationship was found between K_d and K_{f-ads} and the other characteristics of the soil (pH, clay, and CEC). However, the lack of correlation with pH values probably occurred because the pH values of the soils no. 1, no. 3, and no. 4 were in every case much higher than the pK_a of imazosulfuron ($pK_a = 4.0$), allowing the existence of a negligible percentage of the herbicide neutral form.

To confirm the dependence of adsorption on organic matter, the adsorption of imazosulfuron was studied after treating soil no. 4 with hydrogen peroxide. As shown in Table 3, the affinity of the herbicide was lower for the soil treated than for the untreated one.

Table 2. Freundlich Parameters, Distribution Coefficients and Koc Values for Imazosulfuron Adsorption

soils	K_{f-ads}	$1/n_{\rm f-ads}$	r^2	SD	K_d^a	K _{OC} ^a
sandy loam no. 1 sandy loam no. 2 sandy clay loam no. 3 sandy clay no. 4	$\begin{array}{c} 1.46 \pm 0.33 \\ 2.81 \pm 0.58 \\ 3.83 \pm 0.69 \\ 3.02 \pm 0.50 \end{array}$	$\begin{array}{c} 1.02 \pm 0.03 \\ 1.64 \pm 0.12 \\ 1.02 \pm 0.02 \\ 0.60 \pm 0.07 \end{array}$	0.987 0.925 0.985 0.998	0.088 0.096 0.060 0.032	1.64 1.25 3.75 1.74	117 208 98.7 102

^{*a*} Measured at an initial concentration of 4.6 μ g/mL.

Table 3. Distribution Coefficients for ImazosulfuronAdsorption at Different Organic Matter Contents and pHValues for Sandy Clay Soil No. 4

pH ^a	OC (%)	OM (%)	imazosulfuron sorbed ^b (%)	K _d
7.5 ± 0.1	1.70	2.89	6.63	1.76
7.4 ± 0.1	1.30	2.21	6.02	1.60
7.4 ± 0.1	0.77	1.31	3.54	0.91
4.4 ± 0.1	1.70	2.89	20.8	6.58
2.5 ± 0.1	1.70	2.89	80.3	102

^{*a*} Measured in 1:2.5 (w/w) soil/KCl aqueous solution (1M). ^{*b*} Initial concentration 4.8 μ g/mL. ^{*c*} Organic matter calculated as OM (%) = 1.72OC(%).

Table 4. Effect of pH on Imazosulfuron Adsorption

soils	pH ^a	imazosulfuron sorbed ^b (%)	K _d
sandy loam no. 1	2.4 ± 0.1	69.7	58
sandy loam no. 2	2.3 ± 0.1	53.4	29
sandy clay loam no. 3	1.8 ± 0.1	88.5	192
sandy clay no. 4	2.5 ± 0.1	80.3	102

 a Measured in 1:2.5 (w/w) soil/KCl aqueous solution (1M). b Initial concentration 4.8 $\mu g/mL$

Table 5. Distribution Coefficients for ImazosulfuronAdsorption on Soil No. 3 at Different Percentages ofAcetonitrile in the Aqueous Solution

acetonitrile (%)	imazosulfuron sorbed ^a (µg/g)	Kd	acetonitrile (%)	imazosulfuron sorbed ^a (µg/g)	Kd
0.8	17.5	3.9	2.0	9.0	1.9
1.2	12.0	2.6	4.0	8.0	1.7

^{*a*} Initial concentration 4.8 μ g/mL.

The effect of pH on imazosulfuron adsorption by soil was examined by determining K_d values in pH-modified soils (Table 4). Herbicide adsorption increased as the pH of the soil decreased, as expected on the basis of the interaction between acidic ionizable molecules and organic matter (Nicholls and Evans, 1991). The data reported in Table 3 suggest that the increase in adsorption with increasing acidity exceeds the decrease in adsorption due to the reduction of organic matter. These results might explain the $K_{\rm f-ads}$ values of soil no. 2. In fact, even though this soil had the lowest organic carbon content, it adsorbed much more than soil no. 1 because its pH value (pH = 4.5) was similar to imazosulfuron pK_a (4.0). The negligible adsorption of soil no. 1 (pH = 7.0) seems to be reasonable (Shea, 1986; Borggaard and Streibig, 1989; Walker et al., 1989) since imazosulfuron, at this soil pH value, was predominantly in the anionic form and would be repelled by the negatively charged clay particles (Alvarez-Benedì et al., 1998).

Table 5 summarizes the variation of the K_d values obtained for soil no. 3 with aqueous imazosulfuron solutions containing different percentages of acetonitrile (0.8–4% of acetonitrile for a 4.8 μ g/mL imazosulfuron solution). K_d decreased as organic solvent content increased. These results are in agreement with those of several authors (Rao et al., 1985; Arienzo et al., 1993; Bobè et al., 1997). Many hypotheses have been proposed

to explain this phenomenon, e.g. a significant increase in the solubility of imazosulfuron in binary solvent, direct competition between the herbicide and the solvent for adsorption sites, alteration of the soil nature, and the physicochemical properties of the aqueous solution.

The Freundlich equation (eq 1) well-describes the desorption data for imazosulfuron. Desorption data, as obtained by the dilution method, were fitted to the linearized form of the Freundlich equation; the respective constants for desorption are listed in Table 6. As shown in Table 6, $1/n_{\rm f-ads} \gg 1/n_{\rm f-des}$, indicating that a significant amount of the imazosulfuron sorbed is not easily desorbed and that desorption cannot be predicted on the basis of adsorption isotherms.

The magnitude of the hysteresis effect was evaluated (eq 4), and the values spanned a range of 1.8-17.0(Table 6). This indicates an important hysteresis effect, unlike other sulfonylureas-such as chlorsulfuron and chlorimuron-which show slight hysteresis in the adsorption process (Mersie and Foy, 1986; Reddy et al., 1995). In particular, these values indicate that the irreversibility of the desorption process increases with higher equilibrium starting point concentrations, since the hysteresis effect is minimized at low adsorption concentrations. An exception to this is represented by soil no. 3, since its hysteresis coefficient decreases at the highest imazosulfuron concentration. Desorption hysteresis has been reported for a large number of soilorganic compound systems, and several explanations have been proposed for this phenomenon (Clay and Koskinen, 1990; Pavlostathis and Mathavan, 1992), such as chemical or biological transformation, nonequilibrium conditions, and high-energy bonding. However, there was no chromatographic evidence of degradation during the desorption experiments. Furthermore, the methods used to perform the experiments (e.g. equilibration time of 24 h) make the nonequilibrium hypothesis very unlikely, whereas the high-energy bonding hypothesis better suited this case.

Bound residues may be defined as the fraction of the total amount of herbicide initially applied to the soil that cannot be extracted by the method commonly used in residue analyses. The initial adsorption of herbicide by the soil may be irreversible so that the compound cannot be recovered by the usual extraction methods (Gilchrist et al., 1993).

This hypothesis could partly explain the interesting feature of soil no. 3 at the highest imazosulfuron solution concentration (Figure 4). The adsorption– desorption cycle of soil no. 3 showed not only a much higher adsorption capacity but also the ability to desorb the greatest amounts of imazosulfuron at higher concentrations. The slope of desorption isotherm for soil no. 3, which indicates its desorption intensity, was much higher than for the other soils $(1/n_{f-des} = 2.13)$. Accordingly, the value of the hysteresis coefficient was much lower (H = 0.48). However, noteworthy is that the linearized form of the Freundlich equation fitting these data showed a quite low correlation coefficient ($r^2 =$

Table 6. Freundlich Parameters and Hysteresis Coefficient, $H = (1/n_{f-ads})/(1/n_{f-des})$, for Imazosulfuron Desorption

		for given soil				
Freundlich param	initial soln concn (ppm)	sandy loam no. 1ª	sandy loam no. 2 ^a	sandy clay loam no. 3ª	sandy clay loam no. 3 ^b	sandy clay no. 4 ^a
$ \begin{array}{c} K_{f-des(1)} \\ 1/n_{f-des(1)} \\ r^2 \\ (1/n_{f-ads})/(1/n_{f-des}) \end{array} $	4.6	$3.43 \pm 0.09 \\ 0.39 \pm 0.03 \\ 0.99 \\ 2.6 \\ 5.75 \pm 0.25$	$3.02 \pm 0.04 \\ 0.34 \pm 0.01 \\ 0.99 \\ 4.8 \\ 4.62 \pm 0.17$	$12.80 \pm 0.18 \\ 0.12 \pm 0.01 \\ 0.98 \\ 8.5 \\ 29.10 \pm 0.35$		$\begin{array}{c} 4.71 \pm 0.30 \\ 0.33 \pm 0.05 \\ 0.95 \\ 1.8 \\ 6.61 \pm 0.70 \end{array}$
$\frac{R_{f-des(2)}}{1/n_{f-des(2)}}$ $\frac{R^2}{(1/n_{f-ads})/(1/n_{f-des})}$	0.5	5.73 ± 0.23 0.21 ± 0.02 0.97 4.8	$\begin{array}{c} 4.02 \pm 0.17 \\ 0.23 \pm 0.02 \\ 0.98 \\ 7.1 \end{array}$	$\begin{array}{c} 23.10 \pm 0.33 \\ 0.06 \pm 0.01 \\ 0.97 \\ 17 \\ 17 \end{array}$		0.01 ± 0.70 0.20 ± 0.06 0.86 3
$egin{array}{l} { m K_{f-des(3)}} \ { m 1/n_{f-des(3)}} \ { m R}^2 \ { m (1/n_{f-ads})/(1/n_{f-des})} \end{array}$	17.8	$7.93 \pm 0.42 \ 0.19 \pm 0.02 \ 0.97 \ 5.4$	$25.60 \pm 0.50 \ 0.14 \pm 0.01 \ 0.99 \ 11.7$	$egin{array}{c} 6.70 \pm 0.54 \ 2.13 \pm 0.30 \ 0.82 \ 0.48 \end{array}$	17.40 ± 0.37 0.06 ± 0.01 0.97 17	$\begin{array}{c} 12.30 \pm 0.22 \\ 0.12 \pm 0.01 \\ 0.99 \\ 5 \end{array}$

^a Values calculated after four steps. ^bValues calculated for the last three of five steps.



Figure 4. Adsorption–desorption isotherms of imazosulfuron in sandy clay loam soil no. 3.

0.82). Therefore, on the basis of the fifth step considered for the desorption cycle of soil no. 3, the occurrence of a two-stage desorption cycle cannot be excluded. Taking into account the last three of the five steps of the desorption cycle, a much lower slope value $(1/n_{f-des} =$ 0.06) and a much higher hysteresis coefficient (H = 17)were obtained. Data were closer to those observed for soil no. 3 at lower concentrations. Considering the first three and the last three points of the desorption cycle separately yielded Freundlich equations with much higher correlation coefficients ($r^2 = 0.9996$ and $r^2 =$ 0.9760, respectively). This result seems to confirm the hypothesis of bound residues. It seems that after adsorption, some imazosulfuron residues are strongly bound to the soil. Only the fraction of herbicide weakly bound to soil could be easily released during desorption. This fraction seems to be strongly dependent on initial solution concentration, indicating that high-energy binding sites are limited, and progressive saturation of those sites occurs as the solute concentration increases.

The results indicate that the adsorption of imazosulfuron by soil is low, similar to that of other sulfonylurea herbicides, and the most important among the parameters studied were pH and the organic matter content of soil. Further studies are necessary to clarify the nature of binding forces acting on imazosulfuron adsorption by soil.

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