Azimsulfuron Sorption–Desorption on Soil

Alba Pusino,*,† M. Vittoria Pinna,† and Carlo Gessa‡

Dipartimento di Scienze Ambientali Agrarie e Biotecnologie Agro-Alimentari, Università di Sassari,
Viale Italia 39, 07100 Sassari, Italy, and Dipartimento di Scienze e Tecnologie Agro-Ambientali,
Università di Bologna, Viale Fanin 40, 40127 Bologna, Italy

The sorption and desorption of the herbicide azimsulfuron, *N*-[[(4-dimethoxypyrimidin-2-yl)amino]-carbonyl]1-methyl-4-(2-methyl-2*H*-tetrazole-5-yl)1*H*-pyrazole-5-sulfonamide, were studied using five soils. Sorption isotherms conformed to the Freundlich equation. It was found that pH is the main factor influencing the sorption and that the sorption on soils was negatively correlated with pH. The highest level of sorption was measured on soils with low pH and high organic carbon content. Moreover, inorganic soil colloids, for example, smectite clay minerals and iron oxides, contributed to the sorption of azimsulfuron. Desorption was hysteretic on soils with high organic and inorganic colloid contents.

INTRODUCTION

Azimsulfuron (trade name Gulliver, **Figure 1**) is a sulfonylurea herbicide for the postemergence control of *Echinochloa* species, broadleaf and sedge weeds in rice production. The herbicide inhibits the activity of acetolactate synthase (ALS), which is an essential enzyme in the biosynthesis of the branched-chain amino acids, valine, leucine, and isoleucine (*1*). ALS-inhibiting herbicides are characterized by low application rates. Azimsulfuron controls key weeds at a rate of 6−25 g of active ingredient per hectare.

The most significant degradation mechanisms for azimsulfuron are metabolism in soil and indirect photolysis (*2*). Nonsterile soils gave faster rates of degradation than sterile soils, demonstrating the importance of microbial activity in the degradation.

Herbicides used in paddy fields during the flooding season can easily cause pollution through runoff into rivers if they persist longer than the holding period of the water in the paddy. In addition to degradation, sorption from aqueous solution onto solid soil surfaces is a key process in determining the transport and distribution of an organic contaminant in the environment.

The sorption behavior of several sulfonylureas has been previously reported (*3−9*). Sulfonylureas generally exhibit low sorption in laboratory studies, and their sorption extent is negatively correlated with pH. The highest levels of sorption were measured on soils with low pH and high organic carbon and/or clay contents.

Azimsulfuron, like other sulfonylureas, is a weak acid. It is expected to exist predominantly in the anionic form in most agricultural soils; therefore, it has the potential to exhibit
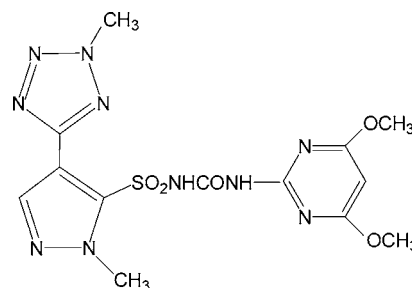
Water solubility (20 °C)		K_{ow} (25 °C)	
pH 5	72 mg L^{-1}	pH 5	4.43
pH 7	1050 mg L^{-1}	pH 7	0.043
pH 9	6540 mg L^{-1}	pH 9	0.0084

Figure 1. Chemical structure and selected physicochemical properties of azimsulfuron.

significant mobility. Relatively little information is available in the literature about its sorption in soils under either laboratory or field conditions (*2, 10*). Knowledge of sorption parameters is essential to estimate the persistence and mobility of azimsulfuron in the soil system.

The aim of this study was to ascertain the influence of soil properties on the sorption and desorption behavior of azimsulfuron. For this purpose, the study was carried out using a range of soils with different properties.

MATERIALS AND METHODS

Materials. Azimsulfuron (99.7% purity) was supplied by DuPont de Nemours France SA (Centre Europeen de Recherches), Nambsheim, France. Its purity was checked by high-performance chromatography (HPLC). Azimsulfuron is a weak acid with a pK_a value of 3.6 (*2*). Its water solubility and octanol/water partition coefficients (K_{ow}) are dependent on pH as shown in **Figure 1** (*2*). The solvents were of HPLC

* Author to whom correspondence should be addressed [telephone (39) 79-229219; fax (39) 79-229276; e-mail pusino@uniss.it].
† Università di Sassari.
‡ Università di Bologna.

Azimsulfuron Sorption–Desorption on Soil

J. Agric. Food Chem., Vol. 52, No. 11, 2004   **3463**

Table 1. Selected Physical and Chemical Properties of Investigated Soils

property	Vercelli	Fornace	Chilivani	Bassona	Monghidoro
OM (%)	1.0	1.3	2.3	4.4	6.3
clay (%)	8.0	18.0	32.0	61.0	20.0
sand (%)	72.0	57.0	32.0	21.0	58.0
silt (%)	20.0	25.0	33.0	18.0	22.0
pH[a]	7.3	7.8	8.6	7.6	5.4
Fe[b]	5.5	6.1	10.2	9.9	8.3
CEC[c]	11.0	17.5	23.0	51.2	23.5

[a] Soil/water = 1:1. [b] Oxalate extractable (g/kg). [c] cmol/kg.

Table 2. Mineralogical Composition of Soils Investigated

composition	Fornace	Chilivani	Bassona	Monghidoro
smectite (%)	12	22	46	3
illite (%)	42	41	32	
chlorite (%)		11	9	34
kaolinite (%)	24	12	7	3
quartz (%)		4	6	53
potash feldspar (%)	22	10		7

Figure 2. Sorption isotherms on natural soil.

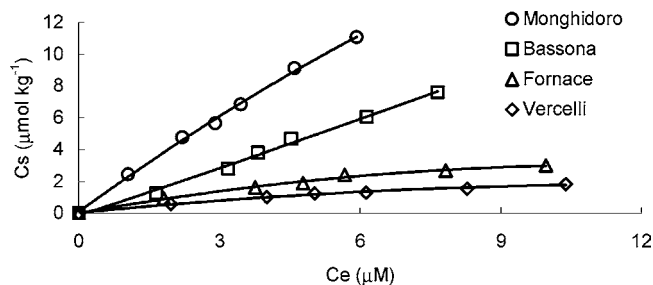grade (Carlo Erba Reagenti, Milano, Italy) and were used without further purification.

Five Italian soils, a sandy loam from Fornace (Emilia-Romagna), a clay loam from Bassona (Emilia-Romagna), a loamy sand from Monghidoro (Emilia-Romagna), a sandy loam from Vercelli (Piemonte), and a clay loam from Chilivani (Sardegna), were examined. The samples were air-dried and sieved to <2 mm. The particle size distribution was measured by the Purdue University Soil Testing Laboratory using the pipet method (*11*). The organic carbon content was determined according to the modified Walkley−Black (*12*) method. The cation exchange capacity (CEC) was determined according to the procedure of Hendershot and Duquette (*13*). Ammonium oxalate-soluble Fe was extracted according to the method of Schwertmann (*14*). Soil pH was determined on slurries with a soil/water ratio of 1:1. Selected physicochemical properties of the soils are listed in **Table 1**. The clay mineralogy of all soils, except Vercelli, was determined by X-ray diffraction (XRD) analysis (see **Table 2**).

Humic acid was obtained from Monghidoro soil according to the procedure of Stevenson (*15*). After precipitation, it was centrifuged, redissolved, and precipitated three times, then dialyzed against distilled water until salt-free, and finally freeze-dried.

Sorption on Soil. Azimsulfuron sorption isotherms were obtained using a batch equilibrium method. In general, triplicate samples of 5 g of air-dried soil, sieved through a 2-mm mesh screen, were equilibrated in polyallomer centrifuge tubes with 10 mL of aqueous herbicide solution. The initial concentration of the herbicide ranged between 2.3 and 11.5 μM. The tubes were shaken (end over end) for 16 h at 25 $\pm$ 2 °C. Preliminary batch kinetic studies indicated that pseudo-equilibrium was reached within 7 h and that no changes in concentration occurred after further shaking for 48 h. After equilibration, the suspension was centrifuged at 19000g for 15 min, and the supernatant was pipetted off and analyzed immediately. The amount adsorbed by soil was calculated from the difference between the initial and final concentrations of azimsulfuron in solution. Blanks with initial concentrations of the herbicide ranging between 2.3 and 11.5 μM without soil were prepared and shaken for 16 h at 25 $\pm$ 2 °C. The control samples analyzed did not show any variation of initial concentration. Therefore, adsorption on polyallomer centrifuge tubes and degradation can be excluded.

The effect of the pH of the soil solution on azimsulfuron sorption was examined by using a batch equilibrium method to measure adsorption to soils after the addition of HCl or NaOH. The amount adsorbed was quantified with the same procedure described for natural soils.

Sorption on Humic Acid. Duplicate samples of humic acid (20 mg) were equilibrated at 25 $\pm$ 2 °C in polyallomer centrifuge tubes with 10 mL of aqueous herbicide solution (pH 3.5). Azimsulfuron concentra-

tions before equilibration ranged from 1.5 to 11.9 μM. The tubes were shaken (end over end) for 20 h. After centrifugation, the supernatant solution was removed and analyzed. Azimsulfuron sorption was also studied on humic acid brought to pH 4.6 by the addition of Ca(OH)$_2$. Preliminary kinetic studies indicated that equilibrium was reached and that no degradation took place within the aforementioned times.

Desorption. Immediately after the sorption process, 5 mL of the supernatant solution was withdrawn and the amount of adsorbed herbicide calculated. The remaining slurry was again brought to 10 mL by the addition of 5 mL of water, equilibrated for 24 h, and centrifuged. These steps (supernatant withdrawing and replacing and re-equilibrating) were repeated four times consecutively. The concentration of herbicide in the desorption solutions was determined, and the amount of herbicide adsorbed on the soil after each desorption step was calculated by difference. Each level of dilution thus provided one point to the desorption isotherms.

HPLC Analyses. The concentration of azimsulfuron was determined by HPLC. The system was assembled as follows: a Waters 1515 pump equipped with a Waters 2487 UV−vis programmable detector operating at 240 nm; breeze chromatography software; a μBondapak C$_{18}$ analytical column (10 μm, 3.9 $\times$ 300 mm) eluting with acetonitrile plus water (50 + 50 by volume) previously brought to pH 2.7 with phosphoric acid at a flow rate of 1 mL min^{-1}. The retention time for azimsulfuron under the chromatographic conditions described previously was 6.8 min. The quantitative determination of azimsulfuron was performed by using an external standard. Calculations were based on the average peak areas of the external standard. The detection limit for azimsulfuron was 0.1 mg L^{-1}, as calculated from the concentration of herbicide needed to obtain a detector response that was approximately twice the background signal.

Data Analysis. Sorption−desorption data were fit to the logarithmic form of the Freundlich equation, log C_s = log K_{ads} + 1/n_{ads} log C_e, where C_s (in μmol kg^{-1}) is the amount of herbicide adsorbed by soil or humic acid, C_e (in μM) is the equilibrium concentration in solution, and log K_{ads} and 1/n_{ads} are empirical constants representing the intercept and the slope of the isotherm, respectively. The K_{OM} values were calculated by normalizing the sorption constants K_{ads} with the organic matter (OM) content of the soils investigated according to equation K_{OM} = K_{ads} $\times$ 100/% OM.

The hysteresis coefficient, H, for the sorption−desorption isotherms was calculated according to the formula H = (1/n_{des})/(1/n_{ads}), where 1/n_{ads} and 1/n_{des} are the Freundlich slopes obtained for the sorption and desorption isotherms, respectively (*16*).

RESULTS AND DISCUSSION

Sorption Studies. The sorption isotherms of azimsulfuron on five soils are shown in **Figure 2**. The empirical Freundlich equation described well the sorption behavior of the herbicide ($r \geq 0.989$). The calculated constants K_{ads} and 1/n_{ads} and the coefficients (r) for the linear fit are given in **Table 3**.

No measurable sorption was observed on Chilivani soil at natural pH (8.6). In all cases the isotherms are nonlinear, with slopes (1/n_{ads}) different from unity. In general, 1/n_{ads} values were <1, resembling L-type isotherms (*17*). An L-type curve indicates

3464 *J. Agric. Food Chem.,* Vol. 52, No. 11, 2004

Pusino et al.

Table 3. Freundlich Parameters for the Sorption of Azimsulfuron on Soil

sample	pH[a]	K_{ads}[b]	$1/n_{ads}$[b]	r	K_{OM}
Monghidoro	5.4	2.32 (± 0.21)	0.88 (± 0.10)	0.998	37
Bassona	7.6	0.72 (± 0.11)	1.18 (± 0.07)	0.996	16
Fornace	7.8	0.64 (± 0.11)	0.70 (± 0.03)	0.989	49
Vercelli	7.3	0.40 (± 0.08)	0.66 (± 0.02)	0.990	40
Chilivani	8.6	nd	nd	nd	nd

[a] pH of aqueous suspension. [b] Value in parentheses is the 95% confidence interval.

Table 4. Linear Regression Analyses for Azimsulfuron Sorption (K_{ads}) and Selected Properties of Soils (x)[a]

| property	correl coeff	prob level	intercept	slope
x	r	P	a	b
pH	0.969	0.006	6.14	−0.72
OM (%)	0.820	0.089	−0.17	0.32
CEC	0.073	0.906	0.71	0.04
clay (%)	0.116	0.853	0.96	0.01

[a] For the equation $K_{ads} = a + bx$.

a relatively high azimsulfuron−soil affinity at low concentration; that is, the extent of sorption decreases as the herbicide concentration increases, because it becomes increasingly more difficult for azimsulfuron to find vacant adsorption sites. Only the Bassona soil isotherm showed a value of $1/n_{ads} > 1$, indicating an S-type curve. This shape indicates a low azimsulfuron−soil affinity at low concentration. Sorption becomes easier as the herbicide concentration increases. In most cases this behavior was attributed to the strong competition between the water molecules and the pesticide for the sorption sites (*18*). In certain instances, especially in the sorption of organic compounds, an S-type isotherm may be due to cooperative interactions among adsorbed organic species that stabilize the sorbate and enhance its affinity for the surface (*19*). An inspection of the data listed in **Table 3** indicates that the highest K_{ads} value corresponds to Monghidoro soil, which contains the greatest amount of organic matter. The extent of sorption decreases with decreasing content of organic matter. Chilivani soil is an exception because it shows a negligible affinity for azimsulfuron despite its fairly high content of OM (2.3%). However, the values of the K_{OM} for the five soils are not very close to each other (**Table 3**), as would be expected if organic matter is the main soil parameter responsible for sorption. Linear and multiple regression analyses between selected soil properties and the Freundlich constant, K_{ads}, were conducted (**Table 4**). The highest correlation coefficient was obtained with the soil pH. There is no significant correlation ($P < 0.05$) between K_{ads} and other soil properties. No significant correlations were found by performing a multiple correlation analysis on the sorption data and taking into account two or more soil parameters.

The correlation between K_{ads} and pH is negative, indicating that the extent of sorption increases as the pH decreases. These findings suggest that, most probably, the high sorption observed on Monghidoro soil was more affected by the low pH value of the soil suspension (5.4) than by the high organic carbon content. On the other hand, the high pH value of the Chilivani soil suspension (8.6) could be responsible for the lack of sorption despite the significant amount of organic matter in the soil. To verify this hypothesis, the sorption of azimsulfuron was studied after modification of the soil pH to ca. 6 or 4. A comparison of the sorption extent before and after pH modification showed that azimsulfuron sorption increased as the soil pH decreased

Table 5. Freundlich Parameters for the Sorption of Azimsulfuron on Soil and on Humic Acid at Modified pH Values

sample	pH[a]	K_{ads}[b]	$1/n_{ads}$[b]	r
Monghidoro	6.1	1.85 (± 0.18)	0.74 (± 0.10)	0.993
	4.1	9.52 (± 0.12)	0.81 (± 0.08)	0.997
Bassona	5.9	5.12 (± 0.07)	0.80 (± 0.05)	0.999
	4.2	9.52 (± 0.05)	0.78 (± 0.03)	0.999
Fornace	6.0	0.78 (± 0.13)	0.77 (± 0.08)	0.994
	4.0	0.91 (± 0.18)	0.80 (± 0.10)	0.994
Vercelli	6.1	0.60 (± 0.09)	0.91 (± 0.10)	0.990
	4.0	0.84 (± 0.11)	0.89 (± 0.11)	0.989
Chilivani	6.2	2.87 (± 0.03)	0.97 (± 0.04)	0.997
	4.1	5.9 (± 0.07)	0.96 (± 0.08)	0.995
humic acid	3.5	103.00 (± 1.31)	1.40 (± 0.08)	0.997
	4.6	1.83 (± 0.29)	2.80 (± 0.26)	0.974

[a] pH of aqueous suspension. [b] Value in parentheses is the 95% confidence interval.
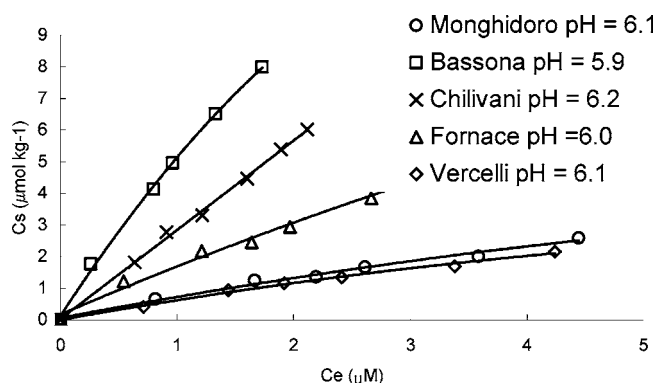
Figure 3. Sorption isotherms on pH-modified soil.

(**Table 5** and **Figure 3**), following the general trend observed for sulfonylureas and weakly acidic herbicides (*20−22*).

Furthermore, it is interesting to note that, in the same range of pH, Bassona soil followed by Chilivani soil, showed the greatest sorption capacities (**Table 5**). These two soils are characterized not only by a fairly good amount of organic matter also by a high clay (mainly of the smectite type, see **Table 2**) and iron oxalate extractable content. The contribution of smectite clay minerals and iron oxides to the sorption of sulfonylureas has been reported several times (*23−25*). In contrast, Monghidoro soil, exhibiting the greatest organic matter content (**Table 2**), a lower iron oxides content, and a negligible smectitic clay content, did not show a high sorption capacity at pH ≈6 and ≈4, suggesting a lower contribution of OM to the overall sorption process of azimsulfuron, at least at this pH value. An examination of the Freundlich constants for the sorption experiments on humic acid extracted from Monghidoro soil at different pH values supports this hypothesis (**Table 5**). Humic acid exhibits a strong affinity for the herbicide at this rather low pH (3.5), but at pH 4.6 it exhibits a much lower affinity for azimsulfuron (**Table 5**). These findings suggest that the organic matter alone cannot explain the level of herbicide sorption observed. The decrease in pH also did not influence significantly the sorptive capacity of Fornace and Vercelli soils that exhibit the lowest amounts of organic and inorganic colloids and the highest sand content among the five soils tested.

In the pH range of soils herein studied, the herbicide ($pK_a = 3.6$) is prevalently in the anionic form; therefore, this is repelled by the negatively charged soil surfaces, which explains the generally low K_{ads} values measured on natural soils. The high sorption level observed on natural Monghidoro soil is most likely due to two combined effects. First, the pH value of the
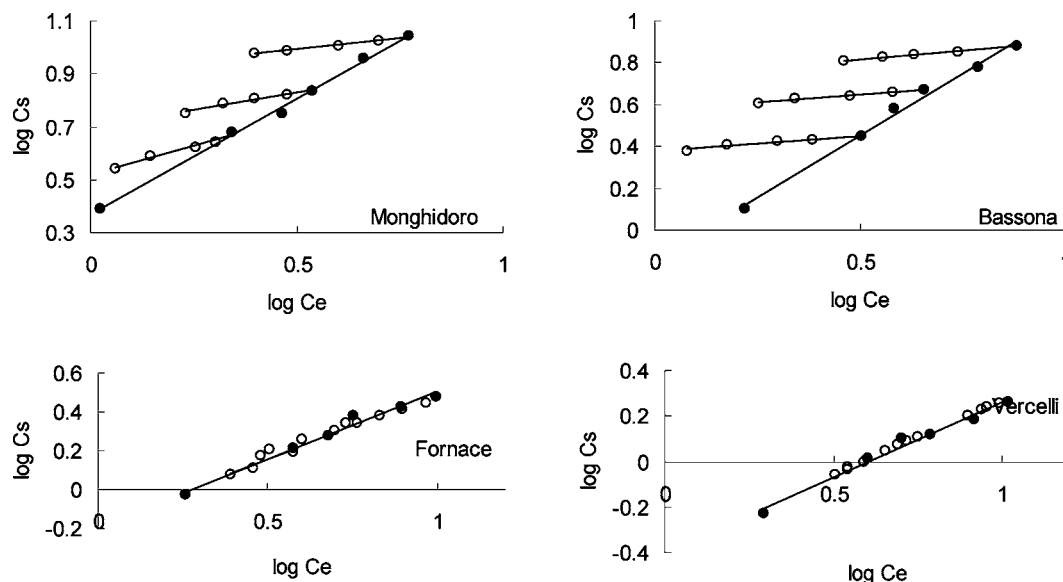
Azimsulfuron Sorption–Desorption on Soil

J. Agric. Food Chem., Vol. 52, No. 11, 2004 **3465**

Figure 4. Freundlich sorption–desorption for azimsulfuron: (●) sorption; (○) desorption.

Table 6. Freundlich Parameters and Hysteresis Coefficients[a] for the Desorption of Azimsulfuron by Soil

	$C_i{}^b$ (μM)	Vercelli[c]	Fornace[c]	Bassona[c]	Monghidoro[c]
K_{des}	4.6	0.40 ($\pm$ 0.05)	0.65 ($\pm$ 0.08)	2.37 ($\pm$ 0.02)	3.29 ($\pm$ 0.09)
$1/n_{des}$		0.66 ($\pm$ 0.09)	0.68 ($\pm$ 0.05)	0.15 ($\pm$ 0.08)	0.43 ($\pm$ 0.03)
r		0.984	0.934	0.982	0.982
H		1.00	0.97	0.13	0.49
K_{des}	6.9	0.50 ($\pm$ 0.07)	0.72 ($\pm$ 0.11)	3.72 ($\pm$ 0.09)	4.97 ($\pm$ 0.01)
$1/n_{des}$		0.54 ($\pm$ 0.04)	0.67 ($\pm$ 0.6)	0.15 ($\pm$ 0.5)	0.26 ($\pm$ 0.07)
r		0.993	0.972	0.980	0.991
H		0.82	0.96	0.13	0.30
K_{des}	11.5	1.79 ($\pm$ 0.14)	0.84 ($\pm$ 0.08)	5.36 ($\pm$ 0.11)	8.11 ($\pm$ 0.21)
$1/n_{des}$		0.51 ($\pm$ 0.09)	0.55 ($\pm$ 0.05)	0.17 ($\pm$ 0.03)	0.17 ($\pm$ 0.12)
r		0.991	0.996	0.995	0.983
H		0.77	0.79	0.14	0.19

[a] Hysteresis coefficient $H = (1/n_{des})/(1/n_{ads})$. [b] Initial concentration. [c] Value in parentheses is the 95% confidence interval.

Monghidoro soil suspension (5.4) is very close to the pK_a value of organic matter, $\sim$5 (25), which makes the organic matter only partly ionized. Therefore, azimsulfuron can overcome, at least partially, the electrostatic repulsion and be adsorbed. However, the interaction between ionic species and organic matter surfaces is well-known and, according to literature, can involve H-bonding, salt bridges, and van der Waals forces (27, 28). In addition, the lower solubility of azimsulfuron in water at pH 5.4 could contribute to the higher sorption level.

Desorption. The parameters for azimsulfuron Freundlich desorption are presented in **Table 6**. **Figure 4** shows the azimsulfuron desorption isotherms in soil at different C_i values. The $1/n_{ads}$ values are greater than $1/n_{des}$, suggesting that the azimsulfuron sorption by soil was not reversible. Hysteresis coefficients, H, were calculated and are listed in **Table 6**. A value of H close to 1 means that the desorption proceeds as quickly as sorption does; therefore, hysteresis is absent. On the other hand, a value of $H < 1$ indicates that the rate of desorption is lower than the rate of sorption and that hysteresis takes place. The highest hysteresis coefficient was observed for Fornace and Vercelli soils, which have a low sorption capacity and a low hysteresis effect, indicating that the small azimsulfuron amount adsorbed is readily desorbed. This behavior is due to their high sand content and low amount of organic and inorganic colloids. In the more sorptive Monghidoro soil some hysteresis is

observed. Low desorption levels observed in sorptive soil were attributed to irreversible bonding between the pesticide molecule and soil colloids, particularly organic matter surfaces (29). An interesting feature of Monghidoro soil is that hysteresis coefficients increase with decreasing azimsulfuron concentration, suggesting that desorption is favored at low sorption levels of herbicide. This finding could indicate that high-energy binding sites are filled only at higher solute concentrations. The highest hysteresis effect (lowest hysteresis coefficient) was observed in Bassona soil, which otherwise showed a low sorption capacity. Moreover, for this soil, hysteresis coefficients were not dependent on the initial amount of azimsulfuron adsorbed. This suggests that, whatever the level of initial azimsulfuron concentration, mainly the high-energy binding sites are occupied by herbicide. Often desorption hysteresis is an artifact due to several phenomena, for example, chemical or biological degradation or nonequilibrium conditions. However, according to preliminary studies, in this case the bulk of the equilibration was complete within 24 h. In addition, on the basis of published kinetic data (2), chemical and microbial degradation is negligible over the pH range (5.4–8.6) and time investigated.

Conclusions. The results indicate that the sorption of azimsulfuron on soil is largely influenced by pH and soil colloid content. Because of its low pK_a value, azimsulfuron occurs mainly in dissociated form in agricultural soils. Therefore, organic matter will be important in the adsorption only if the herbicide is at least partly in the neutral (undissociated) form.

On the whole, these findings demonstrate that azimsulfuron behaves similarly to other sulfonylureas, which are prevalently adsorbed in the undissociated form. Indeed, if the same soil is considered, the sorption extent increases with increasing pK_a value of the herbicide (9, 30).

The surfaces of oxides or expandable clay minerals (as smectites) can contribute to azimsulfuron retention by soil. The sorption of herbicide on soils rich in colloidal components is not reversible. However, depending on the characteristics of soil colloid, different mechanisms involving bonds of different energies may take part in the binding process. Further studies are necessary to clarify the role of the different soil components in azimsulfuron sorption on soil.

3466 *J. Agric. Food Chem.,* Vol. 52, No. 11, 2004

Pusino et al.

LITERATURE CITED

(1) Marquez, T.; Joshi, M. M.; Pappas Fader, T.; Massasso, W. Azimsulfuron (DPX-A8947)—a new sulfonylurea for post-emergence control of *Echinochloa* species, broadleaf and sedge weeds for southern European rice production. *Proc. Br. Crop Prot. Conf.−Weeds* **1995**, *1*, 55−62.

(2) Barefoot, A. C.; Armbrust, K.; Fader, T.; Kato, Y.; Sato, K. Processes affecting the degradation of azimsulfuron in rice paddies. *Proc. 10th Symp. Pestic. Chem.* **1996**, 97−104.

(3) Mersie, W.; Foy, C. L. Adsorption, desorption and mobility of chlorsulfuron in soils. *J. Agric. Food Chem.* **1986**, *34*, 89−92.

(4) Schneiders, G. E.; Koeppe, M. K.; Naidu, M. V.; Horne, P.; Brown, A. M.; Mucha, C. F. Fate of rimsulfuron in the environment. *J. Agric. Food Chem.* **1993**, *41*, 2404−2410.

(5) Vicari, A.; Zimdahl, R. L.; Cranmer, B. K.; Dinelli, G. Primisulfuron and rimsulfuron degradation in aqueous solution and adsorption in six Colorado soils. *Weed Sci.* **1996**, *44*, 672−677.

(6) Álvarez-Benedí, J.; Cartón, A.; Fernandez, J. C. Sorption of tribenuron-methyl, chlorsulfuron, and imazamethabenz-methyl by soils. *J. Agric. Food Chem.* **1998**, *46*, 2840−2844.

(7) Cavanna, S.; Garatti, E.; Rastelli, E.; Molinari, G. P. Adsorption and desorption of bensulfuron-methyl on Italian paddy field soils. *Chemosphere* **1998**, *37*, 1547−1555.

(8) Morrica, P.; Barbato, F.; Giordano, A.; Seccia, S.; Ungaro, F. Adsorption and desorption of imazosulfuron by soil. *J. Agric. Food Chem.* **2000**, *48*, 6132−6137.

(9) Pusino, A.; Fiori, M. G.; Braschi, I.; Gessa, C. Adsorption and desorption of triasulfuron by soil. *J. Agric. Food Chem.* **2003**, *51*, 5350−5354.

(10) Cavanna, S.; Novotny, E.; Molinari, G. P. Bensulfuron-methyl and azimsulfuron adsorption on montmorillonite and kaolinite. *Book of Abstracts*, Royal Society of Chemistry and The International Union of Pure and Applied Chemistry 9th International Congress, Pesticide Chemistry: The Food−Environment Challenge; 1998; Vol. 2, 6D-036.

(11) Day, P. R. Particle fractionation and particle-size analysis. In *Methods of Soil Analysis*; Black, C. A., Ed.; American Society of Agronomy: Madison, WI, 1965; Part I, pp 545−566.

(12) Jackson, M. L. Organic matter determination for soils. In *Soil Chemical Analysis*; Prentice Hall: Englewood Cliffs, NJ, 1958; pp 219−222.

(13) Hendershot, W. H.; Duquette, M. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci. Soc. Am. J.* **1986**, *50*, 605−608.

(14) Schwertmann, U. Differenzierung der Eisenoxide des Bodens durch Extraktion mit saurer Ammoniumoxalat-Lösung (Differentiation of iron oxide in soils by extraction with acid ammonium oxalate). *Z. Pflanzen. Dueng. Bodenkd.* **1964**, *105*, 194−202.

(15) Stevenson, F. J. Organic matter reactions involving herbicides in soil. *J. Environ. Qual.* **1972**, *1*, 333−339.

(16) Barriuso, E.; Laird, D. A.; Koskinen, W. C.; Dowdy, R. H. Atrazine desorption from smectites. *Soil Sci. Soc. Am. J.* **1994**, *58*, 1632−1638.

(17) Giles, C. H.; MacEwan, T. H.; Nakhwa, S. N.; Smith, D. Studies in adsorption: Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *J. Chem. Soc.* **1960**, 3973−3993.

(18) Calvet, R. Adsorption of Organic Chemicals in Soil. *Environ. Health Perspect.* **1989**, *83*, 145−177.

(19) Sposito, G. *The Surface Chemistry of Soils*; Oxford University Press: New York, 1984; pp 1−46.

(20) Beyer, E. M.; Duffy, M. J.; Hay, J. V.; Schlueter, D. D. Sulfonylureas. In *Herbicides: Chemistry, Degradation and Mode of Action*; Kearney, P. C., Kaufmann, D. D., Eds.; Dekker: New York, 1988; Vol. 3, pp 117−190.

(21) Hay, J. V. Chemistry of sulfonylurea herbicides. *Pestic. Sci.* **1990**, *29*, 247−261.

(22) Hamaker, J. W.; Goring, C. A. I.; Youngson, C. R. Sorption and leaching of 4-amino-3,5,6-picolinic acid in soils. *Adv. Chem.* **1996**, *60*, 23−37.

(23) Ukrainczyk, L.; Ajwa, H. A. Primisulfuron sorption on minerals and soils. *Soil Sci. Soc. Am. J.* **1996**, *60*, 460−467.

(24) Calamai, L.; Pantani, O.; Pusino, A.; Gessa, C.; Fusi, P. Interaction of rimsulfuron with smectites. *Clays Clay Miner.* **1997**, *45*, 23−27.

(25) Pusino, A.; Braschi, I.; Gessa, C. Adsorption and degradation of triasulfuron on homoionic montmorillonites. *Clays Clay Miner.* **2000**, *48*, 19−25.

(26) Stevenson, F. J. Organic matter reactions involving herbicides in soil. *J. Environ. Qual.* **1972**, *1*, 333−339.

(27) Khan, S. U. Equilibrium and kinetic studies of the adsorption of 2,4-D and picloram on humic acid. *Can. J. Soil Sci.* **1973**, *53*, 429−434.

(28) Spark, K. M.; Swift, R. S. Effect of soil composition and dissolved organic matter on pesticide sorption. *Sci. Total Environ.* **2002**, *298*, 147−161.

(29) Cox, L.; Koskinen, W. C.; Yen, P. Y. Sorption−desorption of imidacloprid and its metabolites in soils. *J. Agric. Food Chem.* **1997**, *45*, 1468−1472.

(30) Pusino, A.; Petretto, S.; Gessa, C. Sorption of primisulfuron on soil, and inorganic and organic soil colloids. *Eur. J. Soil Sci.* **2004**, *55*, 175−182.