

# Adsorption and Desorption of Imazapyr by Soil

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The adsorption and desorption of imazapyr, ( $\pm$ )-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-pyridinecarboxylic acid, by six soils were studied. Adsorption isotherms conformed to the Freundlich equation. A multiple regression analysis indicated that  $K_{f(ads)}$  values were better correlated if cation exchange capacity and pH ( $r = 0.984$ ) were simultaneously taken into account. The results show that the herbicide adsorption is strongly affected by the pH and the charge of the adsorbing component. The organic matter is effective in imazapyr retention, but only at pH < 5. Enhanced adsorption was observed in amorphous iron oxide, most likely because of a ligand exchange process.

**Keywords:** *Imazapyr; herbicide; adsorption; desorption; Freundlich isotherms; organic matter; iron oxide*

## INTRODUCTION

Imidazolinone herbicides share structural features consisting of the imidazolinone ring attached to an aromatic moiety bearing a carboxylic group. Imazapyr, the most representative member of this class, is a broad-spectrum herbicide for weed control in noncrop areas (Winfield and Bannister, 1988). It is also used to control brush in forestry and plantation crops, such as rubber and oil palm (Boonsirat *et al.*, 1985). Extensive research has been done on this class of herbicides in relation to its mobility in soil and its availability to plants and microorganisms. Among others, Wehtje *et al.* (1987) evaluated the mobility and sorption of radiolabeled imazapyr in five different Alabama soils. The adsorption of the herbicide occurred to the least extent on clay soils and was greatest on a sandy clay loam. Decreases in both the soil water content and soil pH favored the adsorption of the herbicide. In a study on adsorption of imazapyr on eight soils, the order of adsorption was as follows: Sharkey clay loam (AR) > Alberta silt loam (Canada) > Tippeecanoe silt loam (IN) > Sand soil (DE) > Sassafras sandy loam (NJ) > Beardon clay loam (ND) > Plano silt loam (WI) > Buelah loamy sand (AR) (Mangels, 1991). In this case, too, the adsorption was enhanced by a decrease of pH.

As the physical and chemical properties of soils, *e.g.* organic matter and clay content, were not indicated in the above paper, it is not easy to understand why soils with similar textures (*e.g.* Sharkey and Beardon or Alberta and Plano) exhibit remarkably different sorptive features toward imazapyr. Moreover, no information is available concerning the desorption behavior. Because adsorption is among the most important factors in controlling the bioavailability of herbicides in soil, it was of interest to investigate the adsorption and desorption of imazapyr on six soils of various physical and chemical properties. Because of the presence of acid carboxylic and basic pyridine-like functions, imazapyr exhibits amphoteric properties. The behavior of most ionic herbicides in soil is strongly affected by the pH and the nature of the soil colloidal fractions. The effects

of sequential removal of organic matter and of the pH of the soil solution were therefore examined to characterize the mechanisms involved in adsorption. Finally, imazapyr adsorption was correlated to selected soil parameters to identify the soil constituents active in herbicide binding.

## MATERIALS AND METHODS

**Materials.** Imazapyr ( $C_{13}H_{15}N_3O_3$ , aqueous solubility  $11.3 \text{ g L}^{-1}$ ) was supplied by American Cyanamid Co., Princeton, NJ (99.5% purity). Six Italian soils were examined in this study (Table 1). The samples were air-dried and sieved to <2 mm. Particle size distribution was measured by the Purdue University Soil Testing Laboratory using the pipet method (Day, 1965), and organic carbon contents were measured by the modified Walkley–Black method (Jackson, 1958). Cation exchange capacity (CEC) was determined according to the procedure of Hendershot and Duquette (1986). Ammonium oxalate-soluble Fe was extracted according to the method of Schwertmann (1964). Soil pH was determined on slurries with a soil/water ratio of 1:1.

Hydrated ferric oxide was prepared by the dropwise addition of an equivalent amount of  $FeCl_2$  to 250 mL of 2 N KOH with rapid stirring (Landa and Gast, 1973). The fresh precipitate was immediately washed with distilled water and dried under vacuum. It was amorphous according to X-ray analysis and completely soluble in ammonium oxalate (pH 3).

Humic acid was obtained from Macomer soil according to the procedure of Stevenson (1972). After precipitation, it was centrifuged, redissolved and precipitated three times, dialyzed against distilled water until salt-free, and finally freeze-dried.

**Adsorption.** The adsorption of imazapyr was determined at  $25 \pm 2^\circ\text{C}$ . Generally, triplicate samples of 5 g of air-dried soil, sieved through a 2-mm mesh screen, were equilibrated in centrifuge tubes with 20 mL of herbicide solution. Imazapyr concentrations before equilibration ranged from 20 to  $450 \mu\text{M}$ . The tubes were shaken (end-over-end) for 24 h. Preliminary kinetic studies were carried out by adding 4 mL of  $250 \mu\text{M}$  imazapyr aqueous solution to 1 g of soil. At different time intervals (1, 2, 4, 6, 12, and 24 h) samples were removed and centrifuged and the supernatant was analyzed as described below. With all samples 95% of the adsorption took place within the first 5 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 concentration of imazapyr in solution. The effect of

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

property	Torba Histosol clay loam	Coazze Inceptisol loamy sand	Macomer Andosol clay loam	Vercelli Alfisol sandy loam	Cadriano Entisol clay loam	Monte Acuto Cambisol loamy sand
OM (%)	25.60	5.51	16.00	1.45	1.43	2.40
clay (%)	30.68	2.21	14.60	10.77	23.63	9.10
sand (%)	5.09	72.60	32.90	48.56	32.56	70.10
silt (%)	24.86	25.20	26.20	36.83	38.73	16.80
water (%)	12.48	2.22	9.50	2.22	3.25	1.40
pH <sup>a</sup>	4.43	4.72	6.05	6.28	7.40	5.24
CEC <sup>b</sup>	53.32	11.63	17.62	7.68	17.92	4.03
Fe <sup>c</sup>	1.45	0.17	0.57	0.12	0.26	0.19

<sup>a</sup> Soil:water = 1:1. <sup>b</sup> mequiv/100 g. <sup>c</sup> Oxalate extractable (g/100 g).

pH (over the range 3–8) was tested by adding dilute HCl or NaOH, in the absence of the herbicide, and then equilibrating overnight. Sorption was also studied in some soils with reduced organic matter content after treatment with H<sub>2</sub>O<sub>2</sub>. A procedure proposed by Lavkulich and Wiens (1970) was used, modified as follows. To 50 g of soil was added 250 mL of H<sub>2</sub>O<sub>2</sub> (10% by volume). The suspensions were stirred at room temperature until frothing had completely subsided. The samples were then centrifuged and air-dried without any further workup. The treated soils were analyzed for the residual organic matter content.

**Adsorption by Humic Acid and Iron Oxide.** Duplicate samples of humic acid (50 mg), or Ca<sup>2+</sup> humate, and iron oxide (50 mg) were shaken for 24 h with 5 mL of imazapyr solution. The suspension was then centrifuged at 30000g for 15 min. The supernatant was removed and analyzed.

**Desorption.** After the adsorption process, described above, 5 mL of the supernatant was withdrawn and the amount of adsorbed herbicide was calculated. The remaining slurry was again brought to 20 mL by the addition of 5 mL of water, equilibrated for 20 h, and centrifuged. These steps (supernatant withdrawing and replacing, and re-equilibrating) were repeated five successive times. The concentration of herbicides present 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 on the desorption isotherms.

**Imazapyr Analyses.** Herbicide concentrations were determined by high-performance liquid chromatography (HPLC). A Waters 501 liquid chromatograph, equipped with a 300 × 4 mm i.d. Waters  $\mu$ Bondapak C<sub>18</sub> (10  $\mu$ m) analytical column, a multiwavelength Waters 490 programmable detector operating at 250 nm, and a Waters Baseline 810 chromatography workstation, was used. The mobile phase (1 mL min<sup>-1</sup>) was composed of acetonitrile + water + methanol (25 + 70 + 5 by volume, pH 3). In these conditions the retention time of imazapyr was 4.8 min.

**Data Analysis.** The data were fit to the logarithmic form of the Freundlich equation,  $\log C_s = \log K_f + 1/n \log C_e$ , where  $C_s$  (in  $\mu$ mol kg<sup>-1</sup>) is the amount of herbicide adsorbed by soil,  $C_e$  (in  $\mu$ M) is the equilibrium concentration in solution, and  $\log K_f$  and  $1/n$  are empirical constants representing the intercept and slope of the isotherm, respectively. In the case of adsorption on humic acid and iron oxide, the distribution coefficient  $K_d$  was used to measure the adsorption extent. This coefficient is  $C_s/C_e$ , where  $C_s$  (in  $\mu$ mol/100 g) is the amount of herbicide adsorbed and  $C_e$  (in  $\mu$ M) is the equilibrium concentration in solution. Fitting was performed by a least-squares regression analysis program using the Stat View 512 statistical package (Brain Power, Inc., Calabasas, CA) on a Macintosh IIsi computer (Apple Computer). This statistical package was also used to determine the correlation between adsorption and soil parameters.

## RESULTS AND DISCUSSION

**Adsorption Studies.** The empirical Freundlich equation ( $r^2 \geq 0.96$ ) described satisfactorily the adsorption of imazapyr on the soil. The constants  $K_{f(ads)}$  and  $1/n$  determined on our system, together with the coefficients ( $r^2$ ) for the linear fit, are given in Table 2. The

values of  $1/n$  for imazapyr adsorption on all soil samples were  $< 1$ ; in fact, convex or L-type isotherms (Giles *et al.*, 1960) were observed (Figure 1), indicating a relatively high affinity of the herbicide for the sorption sites. An inspection of the data listed in Table 2 indicates that  $K_{ads}$  decreases in the order Torba > Coazze > Macomer > Vercelli > Cadriano > Monte Acuto. Linear regression analyses between  $K$  and selected soil parameters showed the most significant correlation between  $K_{ads}$  and CEC (Table 3).

With the exception of the Monte Acuto soil, the  $K_{f(ads)}$  values decreased with increasing soil pH. Most likely the peculiar behavior of Monte Acuto soil is the result of the rather high content in sand component, which is poorly effective in sorption. However, a poor correlation was found between sorption and soil pH even when the exception was removed from statistical analysis ( $r = 0.681$  and  $p = 0.205$ ).

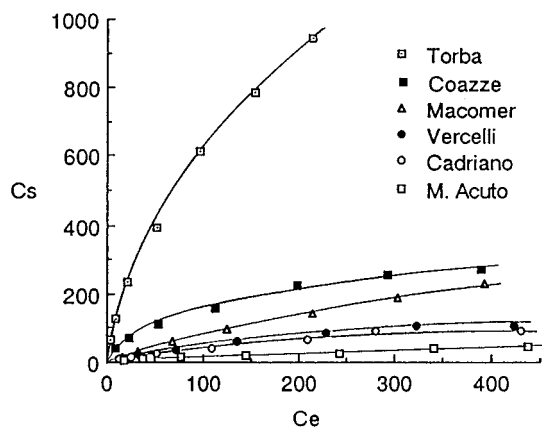
The effect of the pH of the soil solution on imazapyr adsorption was also investigated (Figure 2). It was found that, for a given soil, the herbicide adsorption increased as the pH of the solution decreased, as expected for the interaction of ionizable molecules with organic matter (Nicholls and Evans, 1991). To confirm the dependence of adsorption on organic matter, the adsorption of imazapyr was studied after hydrogen peroxide treatment of Macomer and Monte Acuto soils. Contrary to expectations, as is apparent from the data reported in Table 4, the affinity of the herbicide was higher for oxidized compared with untreated soils. Since the soil peroxidation caused a decrease in the pH of soils (Table 4) because of the formation of low molecular weight acids (Savage and Stevenson, 1961), it is likely that the increase in adsorption due to greater acidity exceeds the decrease in adsorption due to the reduction of organic matter. Support for such a hypothesis is given by an examination of the Freundlich constants for the adsorption isotherms of imazapyr on Macomer and Monte Acuto soils at different values of pH (Table 4). Lowering the pH enhanced significantly the adsorption in these two soils.

Because CEC is a measure of the exchangeable cations in the inorganic and organic fractions, it was thought useful to study the interaction of the herbicide with some colloid components of soil (in Table 5 the adsorption is measured by the distribution coefficient  $K_d$ ). For instance, H humic acid was more effective in adsorption compared with Ca humate, suggesting once again that the pH of the suspension (3.5 for H humic acid and 6.0 for Ca humate) has a great influence on the adsorption of imazapyr. Experiments on amorphous iron oxide emphasized the same pH dependence (Table 5), which indicates that this component exhibits fewer reactive (*i.e.*, protonated) sites as the pH is raised. The findings are in accord with the significant correlation found between imazapyr adsorption coefficient  $K_{f(ads)}$

**Table 2. Freundlich Parameters for the Adsorption,  $K_{f(ads)}$ , and Desorption,  $K_{f(des)}$ , of Imazapyr on Soil**

Freundlich parameter	$C_i^b$ ( $\mu\text{M}$ )	soil					
		Torba	Coazze	Macomer	Vercelli	Cadriano	Monte Acuto
$K_{f(ads)}$		33.24 ( $\pm 0.05$ )	4.56 ( $\pm 0.01$ )	1.91 ( $\pm 0.01$ )	1.68 ( $\pm 0.06$ )	1.47 ( $\pm 0.04$ )	0.84 ( $\pm 0.02$ )
$1/n$		0.63 ( $\pm 0.02$ )	0.50 ( $\pm 0.02$ )	0.81 ( $\pm 0.01$ )	0.71 ( $\pm 0.04$ )	0.72 ( $\pm 0.03$ )	0.65 ( $\pm 0.08$ )
$r^2$		0.999	0.995	0.997	0.990	0.992	0.992
$K_{f(des)}$	80	121.81 ( $\pm 0.09$ )	18.40 ( $\pm 0.08$ )	21.03 ( $\pm 0.04$ )	6.68 ( $\pm 0.09$ )	4.87 ( $\pm 0.04$ )	3.49 ( $\pm 0.11$ )
$1/n$		0.21 ( $\pm 0.07$ )	0.46 ( $\pm 0.04$ )	0.25 ( $\pm 0.01$ )	0.40 ( $\pm 0.01$ )	0.50 ( $\pm 0.07$ )	0.33 ( $\pm 0.04$ )
$r^2$		0.935	0.979	0.945	0.951	0.984	0.967
$1/n_{ads} - 1/n_{des}$		0.42	0.04	0.56	0.31	0.22	0.32
$K_{f(des)}$	150	110.03 ( $\pm 0.11$ )	22.48 ( $\pm 0.09$ )	36.21 ( $\pm 0.14$ )	7.28 ( $\pm 0.04$ )	9.70 ( $\pm 0.07$ )	3.99 ( $\pm 0.01$ )
$1/n$		0.32 ( $\pm 0.06$ )	0.42 ( $\pm 0.01$ )	0.20 ( $\pm 0.01$ )	0.40 ( $\pm 0.04$ )	0.33 ( $\pm 0.02$ )	0.33 ( $\pm 0.02$ )
$r^2$		0.992	0.991	0.966	0.996	0.983	0.992
$1/n_{ads} - 1/n_{des}$		0.31	0.08	0.61	0.31	0.39	0.32
$K_{f(des)}$	250	105.05 ( $\pm 0.03$ )	23.93 ( $\pm 0.03$ )	47.70 ( $\pm 0.14$ )	9.61 ( $\pm 0.06$ )	16.97 ( $\pm 0.10$ )	3.73 ( $\pm 0.08$ )
$1/n$		0.38 ( $\pm 0.01$ )	0.42 ( $\pm 0.01$ )	0.20 ( $\pm 0.01$ )	0.41 ( $\pm 0.01$ )	0.28 ( $\pm 0.02$ )	0.37 ( $\pm 0.01$ )
$r^2$		0.993	0.991	0.964	0.980	0.961	0.982
$1/n_{ads} - 1/n_{des}$		0.25	0.08	0.61	0.30	0.44	0.28
$K_{f(des)}$	350	102.66 ( $\pm 0.05$ )	15.37 ( $\pm 0.06$ )	40.86 ( $\pm 0.11$ )	13.82 ( $\pm 0.05$ )	22.40 ( $\pm 0.12$ )	3.91 ( $\pm 0.02$ )
$1/n$		0.40 ( $\pm 0.01$ )	0.50 ( $\pm 0.03$ )	0.27 ( $\pm 0.02$ )	0.35 ( $\pm 0.01$ )	0.25 ( $\pm 0.02$ )	0.40 ( $\pm 0.02$ )
$r^2$		0.996	0.993	0.978	0.930	0.891	0.982
$1/n_{ads} - 1/n_{des}$		0.23	0	0.54	0.36	0.47	0.27
$K_{f(des)}$	450	99.84 ( $\pm 0.02$ )	19.50 ( $\pm 0.05$ )	51.66 ( $\pm 0.07$ )	24.41 ( $\pm 0.07$ )	29.83 ( $\pm 0.08$ )	6.10 ( $\pm 0.09$ )
$1/n$		0.42 ( $\pm 0.01$ )	0.45 ( $\pm 0.03$ )	0.25 ( $\pm 0.01$ )	0.35 ( $\pm 0.01$ )	0.19 ( $\pm 0.03$ )	0.34 ( $\pm 0.03$ )
$r^2$		0.990	0.975	0.987	0.964	0.805	0.994
$1/n_{ads} - 1/n_{des}$		0.21	0.05	0.56	0.36	0.53	0.31

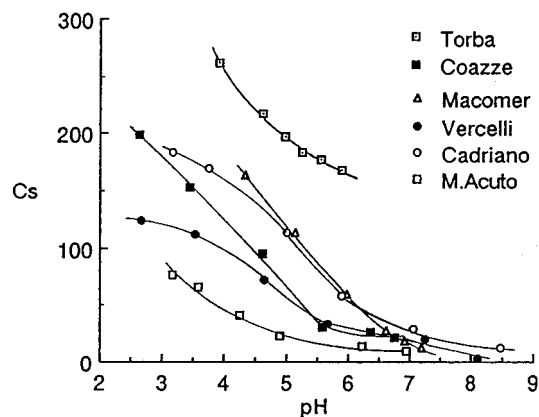
<sup>a</sup> The value in parentheses is the 95% confidence interval. <sup>b</sup> Initial concentration.

**Figure 1.** Adsorption isotherms of imazapyr on soil.  $C_s$  ( $\mu\text{mol kg}^{-1}$ );  $C_e$  ( $\mu\text{M}$ ).**Table 3. Linear Regression Analyses for Imazapyr Adsorption,  $K_{f(ads)}$ , or Desorption,  $K_{f(des)}$ , and Selected Properties of Soils ( $x$ )<sup>a</sup>**

soil parameter $x$	correl coeff $r$	probability level $P$	intercept $a$	slope $b$
adsorption				
OM (%)	0.837	0.038	-2.11	1.08
clay (%)	0.688	0.131	-5.59	0.85
pH	0.598	0.210	46.55	-6.90
CEC	0.953	0.003	-5.50	0.68
Fe <sup>b</sup>	0.941	0.005	-3.54	23.53
desorption				
OM (%)	0.947	0.004	1.40	3.65
clay (%)	0.686	0.130	-16.66	3.04
pH	0.497	0.316	131.23	-17.22
CEC	0.979	0.0007	-6.12	2.11
Fe <sup>b</sup>	0.989	0.0002	-0.86	74.26

<sup>a</sup> For the equation  $K = a + bx$ .  $K_{f(des)}$  values are mean values for different initial concentrations. <sup>b</sup> Oxalate extractable.

and ammonium oxalate-extractable iron or organic matter (Table 3). No significant correlation ( $p > 0.05$ ) was observed between  $K_{f(ads)}$  and other soil properties. Soil pH alone is not correlated to imazapyr adsorption,

**Figure 2.** Effect of pH on the adsorption of imazapyr on soil.  $C_s$  ( $\mu\text{mol kg}^{-1}$ );  $C_i = 160 \mu\text{M}$ .**Table 4. Freundlich Parameters for the Adsorption of Imazapyr at Different Organic Matter Contents and pH Values for Two Soils**

soil	% OM	pH	$K_{f(ads)}$	$1/n$	$r^2$
Macomer	16.00	6.05	1.91	0.81	0.997
	8.76	4.45	5.96	0.88	0.990
	16.00	5.18	6.78	0.84	0.994
	16.00	3.65	20.86	0.82	0.996
Monte Acuto	2.40	5.24	0.84	0.65	0.992
	0.83	3.83	1.28	0.77	0.998
	2.40	4.60	1.47	0.72	0.990
	2.40	3.46	2.20	0.71	0.992

although in all soils the increase of pH decreases the imazapyr adsorption.

As soil properties are frequently interrelated (Burchill *et al.*, 1981), a multiple regression analysis was carried out. The best fit for the imazapyr adsorption by the six soils (with a correlation coefficient of 0.984, significant at the 0.005 probability level) was obtained by taking into account two soil parameters, CEC and pH. Therefore, these two parameters may account for 97% of the total variance. The respective multiple-regression equa-

**Table 5. Imazapyr Adsorption on Humic Acid and Iron Oxide**

system	pH	$K_d^a$
humic acid	3.5	12.37
Ca humate	6.0	3.51
iron oxide	4.8	32.69
iron oxide	7.1	1.70

<sup>a</sup>  $C_e = 100 \mu\text{M}$ .

**Table 6. Imazapyr Desorption by Water<sup>a</sup>**

$C_i^b$ ( $\mu\text{M}$ )	soil					
	Torba	Coazze	Macomer	Vercelli	Cadriano	Monte Acuto
80	15.58	37.22	27.41	37.64	32.73	34.65
150	21.62	36.90	22.81	43.22	38.16	36.92
250	27.08	39.93	23.74	44.64	41.00	38.66
350	27.58	44.73	30.04	42.19	45.08	41.13
450	29.20	42.34	28.87	38.97	42.21	37.01

<sup>a</sup> Percentage of totally initially sorbed herbicide. Values after five desorption steps. <sup>b</sup> Initial concentration.

tion takes the form

$$K_{f(\text{ads})} = 13.512 + 0.608 \text{ CEC} - 3.096 \text{ pH}$$

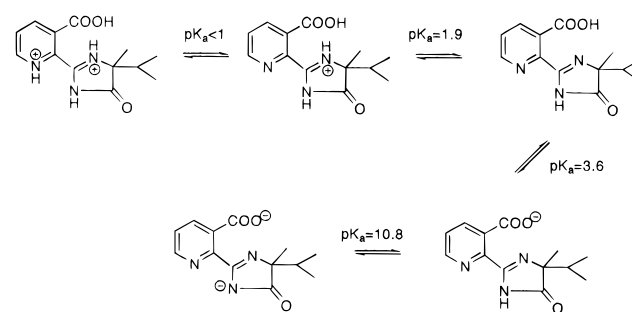
**Desorption Studies.** Desorption data for imazapyr followed the Freundlich equation. The adsorption and desorption data, as obtained by the dilution method, were fitted to the linearized equation of Freundlich, the respective constants for desorption being listed in Table 2. The difference between  $1/n$  values for the adsorption and desorption isotherms (Table 2) is a measure of the extent of hysteresis in desorption. A value of zero means that the desorption proceeds as fast as adsorption does and no hysteresis occurs. The order of desorption hysteresis was Macomer > Cadriano > Vercelli > Monte Acuto > Torba > Coazze.

The cumulative amount desorbed at the end of five desorption steps is given in Table 6. Torba and Macomer soils were the most effective in retaining imazapyr, very likely because of the highest content in iron oxides. This is in agreement with the finding that the most significant correlation is found between the desorption constant and amorphous iron oxide content (Table 3). A further support to the effectiveness of iron oxides in favoring imazapyr retention is provided by the behavior of Coazze and Cadriano samples. These soils, because of their similar iron oxide contents, exhibit a comparable level of desorption, although Coazze contains 3 times the amount of organic matter that Cadriano does. It is observed that hysteresis in adsorption-desorption processes is often an artifact due to degradation or a failure to reach equilibrium (Koskinen and Harper, 1990). However, this can be excluded because, according to preliminary studies, equilibration was complete within 20 h and degradation products were absent at the end of each desorption cycle. Furthermore, increasing the equilibration time from 20 to 44 h did not change the amount of desorbed imazapyr.

## CONCLUSIONS

The results of this study suggest that, depending on the system pH, imazapyr exhibits different adsorption behaviors. Over the measurable pH range, the herbicide exhibits two protonation sites, the carboxylate group and the pyridine-type nitrogen of the imidazolone ring, which dissociate with  $pK_a$  values of 3.6 and 1.9, respectively (Wepplo, 1991). Instead, the lactam group dissociates in water with  $pK_a = 10.8$  (Duda *et al.*,

## Scheme 1



1996). Thus, depending on pH, imazapyr can exist in cationic, neutral, and anionic forms (see Scheme 1). However, in the pH range 4.43–7.40 examined in this study, only the anionic form of imazapyr is available in solution.

The repulsion of the anionic molecule with the negatively charged surfaces explains why the organic matter promotes imazapyr adsorption only in the soils with rather low pH values, *e.g.* Torba and Coazze (pH 4.43 and 4.72, respectively). In fact, the proton dissociation of organic matter, which takes place with  $pK_a$  values around 5 (Stevenson, 1972), reduces the extent of adsorption [see Macomer soil (pH 6.05) rich in organic matter]. The negative pH dependence of imazapyr adsorption observed on organic matter rules out the possibility of a lipophilic interaction between the herbicide and the organic surfaces. However, because of the great solubility of imazapyr in water ( $11.3 \text{ g L}^{-1}$  at  $25^\circ\text{C}$ ) (Worthing and Hance, 1991), this effect was foreseeable.

The zero point charge of amorphous iron oxides occurs around pH 8.5 (Sposito, 1989). Therefore, the iron oxides are the only surfaces provided with a positive charge in the whole pH range of soils studied. The adsorption on iron oxides has been observed for several herbicides, in the anionic form, like 2,4-D (Watson *et al.*, 1973) and quinmerac (Schwandt *et al.*, 1992). Generally, the interaction between anions and the surfaces is attributed to ligand exchange (Kung and McBride, 1989). This is an effective bonding mechanism leading to an inner-sphere complex upon displacement of a hydroxyl group or a water molecule bound to Fe ion by an organic functional group such as a carboxylate. This mechanism may be responsible for the stronger binding properties of soils with a great percentage of iron oxides, *e.g.* Torba and Macomer, which show the lowest desorption extent. The finding is in accord with the high imazapyr adsorptivity observed by Wehtje *et al.* (1987) on Lucedale soil and attributed to the relatively high hematite content.

In conclusion, the results indicate that it is a rather difficult task to state what soil component is effective in imazapyr adsorption by soil. However, it can be supposed that depending on pH the organic matter and/or iron oxides may be effective in the process. Further studies are necessary to clarify the kind of binding mechanisms acting in imazapyr adsorption on soil.

## LITERATURE CITED

- Boonsrirat, C.; Lee, S. C.; Chee, K. S. AC 252,925, a new herbicide for use in rubber plantations. *Proceeding of the 10th Conference of the Asian-Pacific Weed Science Society*, 1985; 99 pp.
- Burchill, S.; Hayes, M. H. B.; Greenland, D. J. Adsorption. In *The Chemistry of Soil Processes*; Greenland, D. J., Hayes, M. H. B., Eds.; Wiley: New York, 1981; pp 221–400.

- 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.
- Duda, A. M.; Dyba, M.; Kozłowski, H.; Micera, G.; Pusino, A. Copper(II) complexes of the imidazolinone herbicide imazapyr. *J. Agric. Food Chem.* **1996**, *44*, 3698–3702.
- 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**, *111*, 3973–3993.
- 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.
- Jackson, M. L. Organic matter determinations for soils. *Soil Chemical Analysis*; Prentice-Hall: Englewood Cliffs, NJ, 1958; pp 219–222.
- Koskinen, W. C.; Harper, S. S. The retention process: mechanisms. In *Pesticides in the Soil Environment: Processes, Impacts, and Modelling*; Cheng, H. H., Ed.; Book Series 2; Soil Science Society of America: Madison, WI, 1990; pp 51–77.
- Kung, K. H.; McBride, M. B. Adsorption of para-substituted benzoates on iron oxides. *Soil Sci. Soc. Am. J.* **1989**, *53*, 1673–1678.
- Landa, E. R.; Gast, R. G. Evaluation of crystallinity in hydrated ferric oxides. *Clays Clay Min.* **1973**, *21*, 121–130.
- Lavkulich, L. M.; Wiens, J. H. Comparison of organic matter destruction by hydrogen peroxide and sodium hypochlorite and its effects on selected mineral constituents. *Soil Sci. Soc. Am. Proc.* **1970**, *34*, 341–346.
- Mangels, G. Behaviour of the imidazolinone herbicides in soil—a review of the literature. In *The Imidazolinone Herbicides*; Shaner, D. L., O'Conner, S. L., Eds.; CRC Press: Boca Baton, FL, 1991; pp 191–209.
- Nicholls, P. H.; Evans, A. A. Sorption of ionisable organic compounds by field soils. Part 1: acids. *Pestic. Sci.* **1991**, *33*, 319–330.
- Savage, S. M.; Stevenson, F. J. Behaviour of soil humic acids towards oxidation with hydrogen peroxide. *Soil Sci. Soc. Am. Proc.* **1961**, *25*, 35–39.
- Schwandt, H.; Kögel-Knabner, I.; Stanjek, H.; Totsche, K. Sorption of an acidic herbicide on synthetic iron oxides and soils: sorption isotherms. *Sci. Total Environ.* **1992**, *123/124*, 121–131.
- Schwertmann, U. Differenzierung der Eisenoxide des Bodens durch photochemische Extraktion mit saurer Ammoniumoxalat-Lösung. (Differentiation of iron oxide in soils by a photochemical extraction with acid ammonium oxalate). *Z. Pflanzen. Dueng. Bodenkd.* **1964**, *105*, 194–202.
- Sposito, G. Soil particle surface. In *The Chemistry of Soils*; Sposito, G., Ed.; Oxford University Press: New York, 1989; pp 136–141.
- Stevenson, F. J. Organic matter reactions involving herbicides in soil. *J. Environ. Qual.* **1972**, *1*, 333–339.
- Watson, J. R.; Posner, A. M.; Quirk, J. P. Adsorption of the herbicide 2,4-D on goethite. *J. Soil Sci.* **1973**, *24*, 503–511.
- Wehtje, G.; Dickens, R.; Wilcut, J. W.; Hajek, B. F. Sorption and mobility of sulfometuron and imazapyr in five Alabama soils. *Weed Sci.* **1987**, 358–864.
- Wepplo, J. Chemical and physical properties of the imidazolinones. In *The Imidazolinone Herbicides*; Shaner, D. L., O'Conner, S. L., Eds.; CRC Press: Boca Baton, FL, 1991; p 18.
- Winfield, R. J.; Bannister, C. J. Imazapyr for broad spectrum weed control in forestry. In *Aspects of Applied Biology*; Association for Applied Biology: Warwick, U.K., 1988; Vol. 16, p 79.
- Worthing, C. R.; Hance, R. J., Eds. *The Pesticide Manual*, 9th ed.; British Crop Council: Bracknell, U.K., 1991; p 486.

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