PLANTA DANINHA

SBCPD
SOCIEDADE BRASILEIRA DA
CIÊNCIA DAS PLANTAS DANINHAS

<http://www.sbcpd.org>

ISSN 0100-8358 (print)
1806-9681 (online)

Article

SORPTION-DESORPTION BEHAVIOR OF IMAZETHAPYR AND IMAZAPIC ON SIX BRAZILIAN SOILS

Comportamento de Sorção-Dessorção do Imazethapyr e do Imazapic em Seis Solos Brasileiros

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ABSTRACT - The characterization of sorption–desorption for imazethapyr and imazapic in six agricultural soils was performed to assess the availability of these herbicides in pollution processes. In this pursuit, the batch equilibrium method and high-performance liquid chromatography were used. The magnitude of K_f values ranging from 0.38 to 2.52 mg^{1-n} kg^{-1} L^n for imazethapyr and 0.43 to 2.72 mg^{1-n} kg^{-1} L^n for imazapic indicate weak sorption in the evaluated soils. Soil pH (5.1 to 6.1) and iron oxalate affect sorption-desorption of both herbicides but the type and percentage of clay can be the main factor affecting these two processes. A high desorption percentage (>70%) was found in Regosol, Dystric Plinthosol, Ferralsol (for both herbicides), and Dystric Gleysol (only imazapic) soils, which implies in leaching risks of these imidazolinone herbicides into groundwater. Lower desorption (<50%) was found in Cambisol and Alisol (for both herbicides), and (~50%) in Dystric Gleysol (only imazethapyr) soils, indicating that these herbicides could potentially injure the sensitive crops grown in rotation.

Keywords: herbicides, imidazolinone, pollution, batch equilibrium.

RESUMO - A caracterização da sorção-dessorção do imazethapyr e do imazapic foi realizada em seis solos agrícolas para avaliação da disponibilidade desses herbicidas nos processos de poluição. Neste propósito, foram utilizados o método de equilíbrio em batelada e a cromatografia líquida de alta eficiência. A magnitude dos valores de K_f, que variaram entre 0,38 e 2,52 mg^{1-n} kg^{-1} L^n para o imazethapyr e entre 0,43 e 2,72 mg^{1-n} kg^{-1} L^n para o imazapic indicam uma sorção fraca nos solos avaliados. O pH do solo (5,1-6,1) e o oxalato de ferro afetam a sorção-dessorção de ambos os herbicidas, mas o tipo e a percentagem de argila podem ser os principais fatores que afetam esses dois processos. Alta percentagem de dessorção (>70%) foi encontrada nos solos Entissolo, Plintossolo Distrófico, Latossolo Vermelho-Amarelo (para ambos os herbicidas) e Gleissolo Distrófico (somente imazapic), o que implica em riscos de lixiviação desses herbicidas imidazolinonas para águas subterrâneas. A dessorção mais baixa (<50%) foi observada no Cambissolo Húmico e no Argissolo Vermelho (para ambos os herbicidas) e (~50%) no Gleissolo Distrófico (apenas imazethapyr), o que indica que esses herbicidas poderiam potencialmente causar danos às culturas de rotação sensíveis.

Palavras-chave: herbicidas, imidazolinonas, poluição, equilíbrio em batelada.

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Received: March 23, 2017
Approved: May 5, 2017

Planta Daninha 2018; v36:e018177486

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Doi: 10.1590/S0100-83582018360100140

INTRODUCTION

Herbicides represent a wide range of properties and chemical groups and have physicochemical characteristic variables affecting their interaction with soil colloids. This interaction results in agronomic efficiency or inefficiency of herbicides, as well as environmental impact with regard to contamination of the soil, surface water, and groundwater by undesirable residues of not-completely degraded herbicides, during the cycle of the main crop (Loux et al., 1989; Stougaard et al., 1990; Loux and Reese, 1993).

Imidazolinone (IMI) herbicides are widely used in agricultural crops of relevant importance to control several weed species, such as red rice (*Oryza sativa* L.) in Clearfield® (IMI-tolerant crops) production systems, and to reduce production costs (Tan et al., 2006; Sudianto et al., 2013). They are widely used because of their low application rates, decreased environmental impact, and selectivity in a wide range of crops. The mechanism of action involves inhibition of the acetohydroxyacid synthase (AHAS) enzyme, responsible for the biosynthesis of branched-chain amino acids (valine, leucine, and isoleucine) in plants that will slowly die because of their inability to synthesize proteins, which are important for cell division (Tan et al., 2006; Silva et al., 2007; Duggleby et al., 2008; Sudianto et al., 2013).

All IMI herbicides have achiral imidazole moiety in their molecular structure, but they differ in structure in the second heterocycle (Figure 1). These herbicides have the presence of two enantiomers as a common characteristic and their biological activity is usually the result of the preferential reactivity of only one enantiomer (Ramezani et al., 2010). The selected physicochemical properties of imazethapyr and imazapic are listed in Table 1.

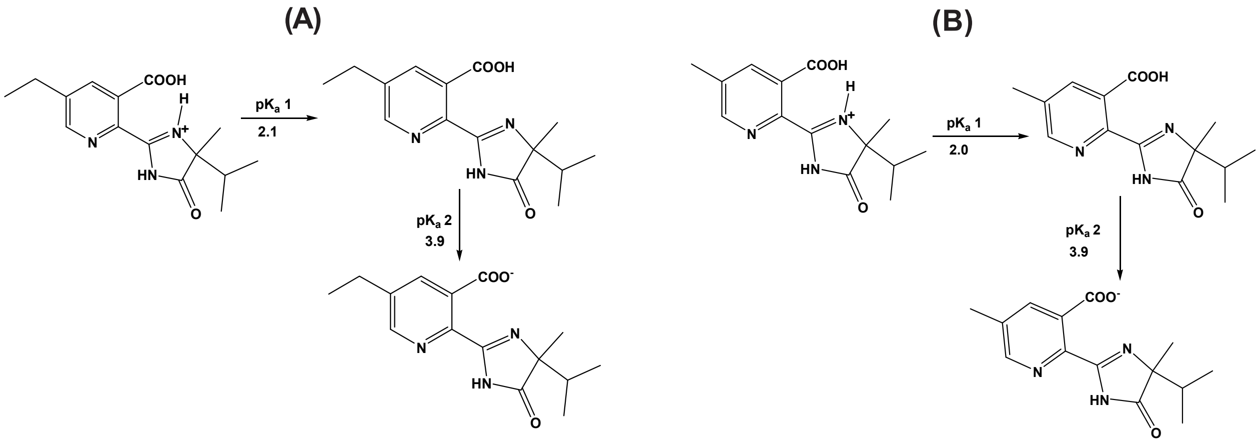

Figure 1 **-** Chemical structures of imazethapyr (A) and imazapic (B); cationic form; neutral form and anionic form.

Table 1 **-** Selected physicochemical properties$^{(1)}$ of imazethapyr and imazapic

Herbicide	Molecular weight (g mol^{-1})	pK$_{a1}$	pK$_{a2}$	Solubility in water (25 °C) (mg L^{-1})	Vapor pressure (60 °C) (Pa)
Imazethapyr	289.3	2.1	3.9	1420	<1.33 x 10^{-5}
Imazapic	275.3	2.0	3.9	2150	< 1.33 x 10^{-5}

(1) Tomlin, C.D.S. 2000. The Pesticide Manual. 12th ed. Surrey, U.K.: British Crop Protection Council.

Sorption controls the availability of herbicides to the plant, the rate of degradation by soil microorganisms (Goetz et al., 1990) and the movement of the chemical through the soil profile (Oliveira Junior et al., 2001; Porfiri et al., 2015). It is usually characterized by using the batch equilibrium method. The sorption coefficient (K_f) obtained for Freundlich isotherms and the sorption coefficient normalized to soil organic carbon (OC) content ($K_{f\text{-}oc}$) have been the most frequently used coefficients for estimation mobility of herbicides.

The intensity and extent of sorption depend on the physicochemical properties of the soil, such as pH (Loux et al., 1993; Bresnahan et al., 2000), organic matter (OM) (Stougaard et al., 1990; Boivin et al., 2005; Ahmad and Rahman, 2009), texture (Loux et al., 1989), moisture and temperature (Goetz et al., 1990; Loux and Reese, 1993) and also the molecular characteristics of the pesticide (Green, 1974; Oliveira Junior et al., 1999).

The amphoteric nature (presence of both acidic and basic functional groups) of IMI herbicides allows them to exist in anionic, neutral or cationic forms, depending upon the pH of the environment. When the soil pH is greater than pKa, the anionic form of these herbicides predominates ($-COO^-$) and this form is weakly bound or repulsed by negative charges of the soil colloids, resulting in low sorption to neutral and high pH soils (Oliveira Junior et al., 2001; Aichele and Penner, 2005; Porfiri et al., 2015). Consequently, soil pH may affect the persistence of the IMI herbicides in the environment, may have carryover effects on sensitive succeeding crops (Gianelli et al., 2014; Souza et al., 2016) and leach to the groundwater (Loux et al., 1989; Oliveira Junior et al., 1999; Regitano et al., 2005).

The reversibility of the sorption process depends on binding bonds, e.g., ionic or covalent bonding, or on weak binding forces, such as Van der Waals' forces or a dipole-dipole interaction, formed between the sorbent surface and the compound molecules (Singh and Kaur, 2013).

In addition to sorption, desorption process of pesticides is also important since it determines the release rate and the potential mobility of pesticides in soil (Koskinen and Harper, 1990; Mamy and Barriuso, 2007). Furthermore, this process may reflect some of the interactions involved between the chemical and the various soils (Wang and Liu, 1999; Boivin et al., 2005).

Particularly, there are very few studies about the desorption behavior of weakly acidic herbicides such as IMI herbicides on tropical soils, e.g., Brazilian soils. Consequently, there is very limited information about the behavior of these herbicides in tropical soils, which are chemically and physically distinct from non-tropical soils (Oliveira Junior et al., 2001).

Taking into account the feature of the IMI herbicides and the very limited information on the behavior of imazethapyr and imazapic in tropical soils, the aim of the present study was to evaluate the sorption-desorption of these herbicides on six soils from Brazil, and their different physicochemical properties, under the same laboratory conditions.

MATERIALS AND METHODS

Soil characteristics

The sorption of herbicides imazapic and imazethapyr was evaluated for six Brazilian soils often used in rice and soybean crops: Ferralsol (LVA), Dystric Plinthosol (FX), Dystric Gleysol (GX) from the Tocantins state, and Cambisol (CH), Alisol (PV), and Regosol (RR) from the Rio Grande do Sul state. Soil samples were collected at a depth of 0 to 20 cm. Then, the samples were homogenized, air-dried, and sieved through a 4 mm mesh. They were then ready to be further characterized. It should be noted that these soils do not have a history of herbicide application.

The physicochemical properties of the soils are listed in Tables 2 and 3. It is considered that a large portion of the total iron (Fe) in soils is frequently found in the form of oxides (Olson, 1965). This property can be useful to consider the sorption of IMI herbicides in the evaluated soils under study.

Chemicals and reagents

Imazapic [(R,S)-5-methyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid] and imazethapyr [(R,S)-5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid] were purchased from Sigma Aldrich (purity greater than 99%). Stock solutions (1000 mg L^{-1}) of each herbicide standard were prepared in HPLC grade acetonitrile, protected from light, and stored in a fridge at 4 °C. Stock solutions of herbicides were further diluted to 10 mg L^{-1} in 0.01 M $CaCl_2$ and stored in a fridge at 4 °C. All solutions were prepared using ultrapure water obtained from a Millipore water purification system (≥18.2. MΩ·cm, Milli-Q, Millipore).

Table 2 **-** Characterization of the mineralogical and chemical properties of the soil samples

Soil	pH (H_2O)	P	K	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	(t)	V	M	OM
		($mg\ dm^{-3}$)		($cmol_c\ dm^{-3}$)					(%)		
LVA	5.7	0.8	79	0.99	0.52	0.00	4.70	1.71	26.7	0.00	3.00
FX	6.1	3.5	27	3.39	1.35	0.00	3.00	4.81	61.6	0.00	2.22
GX	5.2	1.3	82	1.69	0.75	0.57	5.20	3.22	33.8	17.7	2.35
CH	5.2	5.9	99	0.90	0.50	1.70	6.77	3.35	20.0	51.0	2.30
PV	5.2	1.5	27	1.20	0.60	2.10	6.77	3.97	22.0	53.0	2.10
RR	5.1	9.1	115	3.30	0.70	0.70	8.09	4.99	35.0	14.0	5.10

Soil	Iron Oxalate	Dithionite Iron
	(%)	
LVA	0.14	2.19
FX	0.10	1.29
GX	0.56	0.83
CH	0.23	0.92
PV	0.12	2.50
RR	0.13	1.34

Analyses carried out in the Laboratory of Soil Analysis of Viçosa (Minas Gerais State, Brazil), according to the methodology of the Brazilian system of soil classification – EMBRAPA (Empresa Brasileira de Pesquisa e Agropecuária) (2013), (t) = effective cation exchange capacity, V = base saturation, M = Saturation by Al^{+3}; OM = organic matter. According to WRB / FAO (1998): LVA (Ferralsol); FX (Dystric Plinthosol); GX (Dystric Gleysol); CH (Cambisol); PV (Alisol); RR (Regosol). Iron oxides were determined by atomic absorption spectrophotometry.

Table 3 **-** Characterization of the physical and textural properties of the soil samples

Soil	Sand	Silt	Clay	Textural class
	(%)			
LVA	55	6	39	sand clay
FX	47	16	37	sand clay
GX	32	45	23	loam
CH	62	12	26	sand clay loam
PV	42	20	38	clay loam
RR	51	17	32	clay loam

Analyses carried out in the Laboratory of Soil Analysis of Viçosa (Minas Gerais State, Brazil) according to the methodology of the Brazilian system of soil classification – Embrapa (Empresa Brasileira de Pesquisa e Agropecuária) (2013).

Herbicide sorption study

The sorption of imazapic and imazethapyr from the aqueous solution was determined at 25 ± 2 °C by employing the batch equilibrium method, using 0.01 M $CaCl_2$ as a background electrolyte (OECD, 2000). This method involves two sets of measurements, both in triplicate. The first set, for determination of equilibrium time, used solutions with a single concentration of each herbicide (10 mg L^{-1}). Triplicate soil samples (2 g) were equilibrated with herbicide solutions (10 mL) at soil solution ratios of 1:5 by shaking for 0.5; 1; 5; 8; 12; 16; and 24 hours in 50 mL polypropylene tubes. An equilibrium time of 16 hours was found to be sufficient to reach a solution with equilibrium in the study of the LVA, FX, GX, CH, and PV soils (both herbicides). In the case of the RR soil, such time was 16 hours for imazethapyr and eight hours for imazapic. In the second set, the sorption isotherms were obtained for each herbicide from solutions at concentrations of 0.4, 0.8, 1, 5, 10, and 15 mg L^{-1}. At the end of the equilibrium period, the suspension was centrifuged for 10 minutes at 3200 rpm. The supernatant solution was removed and filtered through a Polytetrafluoroethylene (PTFE) membrane (diameter of 25 mm and pore size of 0.45 μm) directly to 2 mL vials.

The concentration of the herbicides in each solution was determined with a Shimadzu LC 20AT high-performance liquid chromatograph (HPLC) attached to a UV/VIS detector (Shimadzu SPD-20A). The following reverse-phase conditions were used for the analysis of these herbicides: C18 reversed phase column (Shimadzu VP-ODS Shim-pack 250 mm x 4.6 mm I.D., 4.6 µm ODS), isocratic mobile phase 40:60 acetonitrile / water (adjusted to pH 3.0 with phosphoric acid) (v/v), flow rate of 1 mL min^{-1}, injection volume of 20 µL, column oven temperature of 25 ^{o}C, and detection wave length of 254 nm. Under these conditions, the retention times of imazapic and imazethapyr were 4.9 and 6.4 minutes, respectively. Quantification was performed by comparing the peak areas with the standard herbicide solutions.

The solutions of 0.01 M $CaCl_2$ (no herbicides under study) were added to each soil and the batch equilibrium method was used to check if there was analytical interference owing to soil extracts for its retention time in the chromatograms.

Herbicide desorption study

The study on desorption was conducted immediately after the sorption experiment by using the soils of this study (containing adsorbed herbicide) at a higher concentration of 15 mg L^{-1}. After addition of $CaCl_2$ (0.01 M, 10 mL) without chemicals, the soils were resuspended in a vortex action shaker and shaken for the equilibrium time evaluated for each soil. The soil suspensions were centrifuged and 1 mL of supernatant was removed for analysis. This was done after the end of each herbicide desorption cycle. After removal of 1 mL of the supernatant, an equal aliquot of the same solution without the IMI herbicides was added to the 50 mL polypropylene tube. The amount of herbicide desorbed at the end of each cycle was quantified and desorption percentages were calculated by using three and four successive desorption cycles for imazethapyr and imazapic, respectively. Determination of the exact percentage of herbicides desorbed in each desorption cycle was based on the amount of these herbicides in the $CaCl_2$ solution after removal of 1 mL of the supernatant and the percentage of herbicides desorbed in the cycles prior to desorption.

Determination of sorption coefficient

The sorption data were fitted to the logarithmic form of the Freundlich equation, whose equation is:

$$log\ C_s = log\ K_f + 1/n\ log\ C_e \qquad \text{(eq. 1)}$$

where C_s is the amount of chemical sorbed by the soil (mg kg^{-1}) and C_e is the equilibrium concentration in the solution (mg L^{-1}).

C_s was calculated from the difference between the amount initially added and C_e. The sorption coefficients (K_f, mg^{1-n} kg^{-1} L^n) were determined from linearized isotherms of Freundlich. K_f and 1/n are empirical constants, which indicate the affinity of the soil for the herbicide and the degree of linearity between the amounts adsorbed and the solution concentration, respectively. Based on the values of C_e and C_s used in the linearized equation of Freundlich for the interpretation of the sorption process, the sorption coefficients were also calculated as functions of organic carbon content (OC) in accordance with the equation:

$$k_{f-OC} = \left(\frac{k_f}{\%OC}\right) \times 100 \qquad \text{(eq. 2)}$$

OC was calculated as follows: *OC* (%) = OM (%) / 1.724, where OM is the organic matter content.

Data analysis

Fitting was performed by a least squares regression analysis program using the Microsoft Excel (2013) and the statistical package SigmaPlot 12. This statistical package was also used to determine the correlation between adsorption and soil parameters.

All data were subjected to regression analysis, and the coefficients of the equations were tested by the *t*-test at 5% significance.

RESULTS AND DISCUSSION

Sorption of imazapic and imazethapyr

Freundlich sorption isotherms of imazapic and imazethapyr were obtained for the six selected soils (Figures 2 and 3). The sorption behavior for herbicides in the soils was on account of the parameter 1/n of the Freundlich model, which depends on the linearity of the isotherm (Giles et al., 1960). In the study, there were significant differences in the values of 1/n for both IMI herbicides in the evaluated soils samples. The Freundlich isotherm coefficients are listed in Tables 4 and 5.

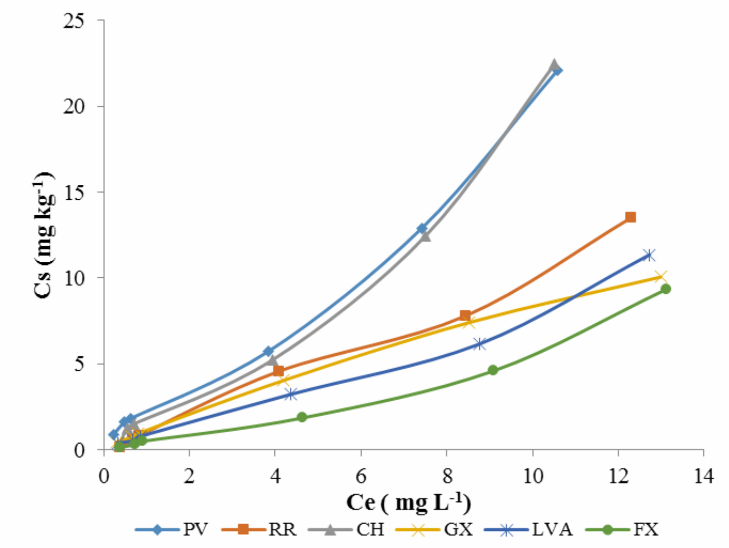

Figure 2 **-** Sorption isotherms of imazapic in the soil samples LVA (Ferralsol), FX (Dystric Plinthosol), GX (Dystric Gleysol), CH (Cambisol), PV (Alisol) and RR (Regosol), at different times.

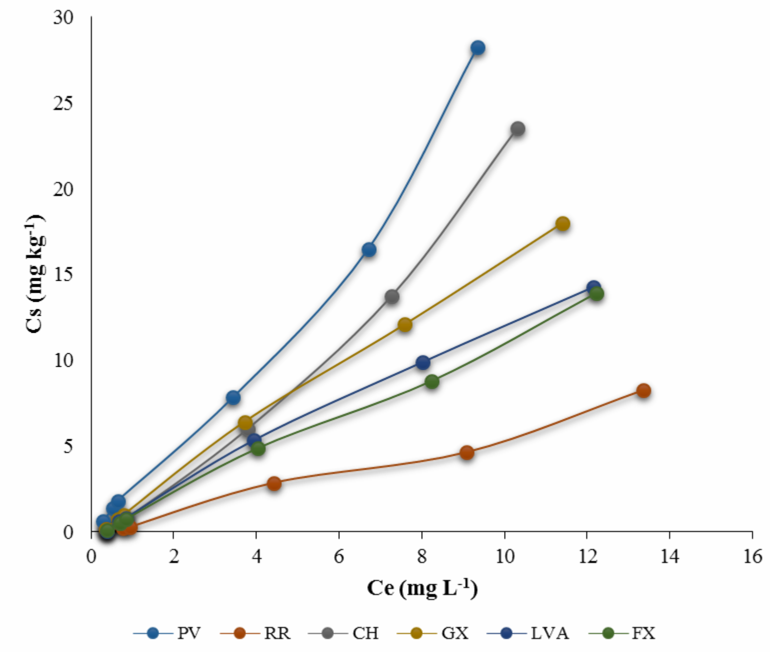

Figure 3 **-** Sorption isotherms of imazethapyr in the soil samples LVA (Ferralsol), FX (Dystric Plinthosol), GX (Dystric Gleysol), CH (Cambisol), PV (Alisol) and RR (Regosol), at different times.

Table 4 **-** Freundlich parameters (K_f and 1/n) and $K_{f\text{-}OC}$ values for the sorption of imazethapyr on the soils

Soil	K_f (mg^{1-n} kg^{-1} L^n)	1/n	R^2	$K_{f\text{-}OC}$ (mg^{1-n} kg^{-1} L^n)	Isotherm type
PV	2.52	1.024	0.994	206.88	C-type
RR	0.38	1.176	0.981	12.84	S-type
CH	0.68	1.564	0.976	50.97	S-type
GX	0.98	1.273	0.968	71.89	S-type
LVA	0.55	1.088	0.893	31.6	C-type
FX	0.64	1.297	0.963	49.7	S-type

* LVA (Ferralsol), FX (Dystric Plinthosol), GX (Dystric Gleysol), CH (Cambisol), PV (Alisol) and RR (Regosol).

Table 5 **-** Freundlich parameters (K_f and 1/n) and $K_{f\text{-}OC}$ values for the sorption of imazapic on the soils

Soil	K_f (mg^{1-n} kg^{-1} L^n)	1/n	R^2	$K_{f\text{-}OC}$ (mg^{1-n} kg^{-1} L^n)	Isotherm type
PV	2.72	0.785	0.980	223.29	L-type
RR	0.70	1.215	0.956	23.66	S-type
CH	1.54	1.079	0.944	115.43	C-type
GX	1.17	0.845	0.998	85.83	L-type
LVA	1.08	0.912	0.986	62.06	L-type
FX	0.43	1.111	0.986	33.39	C-type

LVA (Ferralsol), FX (Dystric Plinthosol), GX (Dystric Gleysol), CH (Cambisol), PV (Alisol) and RR (Regosol).

Based on the values of 1/n, an evaluation can be made of the Freundlich isotherms on the type (L, C and S) and conclusions can be drawn about the behavior of the herbicides in the soil during the sorption process. The IMI herbicides sorption isotherm from the concentrations examined in the present study was of the C-type isotherm for the CH and FX soils for imazapic, and PV and LVA soils for imazethapyr (Figure 3) with 1/n close to 1, which implies that the ratio between the adsorbed concentration in the soil and the part remaining in solution was almost the same at any concentration. In this way, the K_f value increased linearly with herbicide concentration. The soil samples GX, LVA and PV (for imazapic) showed the behavior addressed to the sorption isotherm L-type where 1/n<1. This type of isotherm is characterized by a decreasing slope as the concentration increased, because vacant sorption sites decreased as the adsorbent got covered (Koskinen and Harper, 1990; Koskinen et al., 2006; Oliveira and Brighenti, 2011). This occurred because of the limited ability to form bonds with the colloidal material, and sorption coefficient variation can occur with temperature and soil moisture (Oliveira Junior et al., 2001; Gianelli et al., 2014). Pusino and co-workers (Pusino et al., 1997) evaluated the sorption of the IMI herbicide imazapyr on six soils and found values of 1/n<1 on all soil samples with convex or L-type isotherms, indicating a relatively high affinity of the herbicide with the sorption sites. Gianelli and co-workers [Gianelli et al., 2014] found a C-type isotherm for this same IMI herbicide in one of the evaluated three soils. The imazapic exhibited the sorption isotherm S-type with 1/n>1 for the RR soil, and the imazethapyr for the RR, CH, GX and FX soils, which indicate that the sorption of the IMI herbicide molecules modified the adsorbent surface, favoring future sorption (Oliveira and Brighenti, 2011). An S-type isotherm indicates that the more solutes are already adsorbed (Giles et al., 1960), the easier it is for additional amounts to become fixed. Leone and co-workers (Leone et al., 2001) found this type of isotherm for the IMI herbicide imazaquin. It should be noted that only RR kept the same behavior for both herbicides while the others changed their behavior. For the PV, CH, GX, FX and LVA soils, it can be attributed to soils physicochemical features that interacted with the herbicides.

The sorption characteristics of imazethapyr were investigated in soils and it was found that pH and soil OC were the main predictors of sorption for this herbicide (Ahmad and Rahman, 2009). However, in addition to pH, other factors might have influenced sorption of ionizable compounds in soils, such as clay, Fe, and Al content (Kah and Brown, 2006; Espinoza et al., 2009; Gianelli et al., 2014).

In the case of $pH > pKa_{2,}$ sorption is promoted by the predominance of the anionic form of the herbicides, which is attracted by the positive charge of the surface. According to some authors (Pusino et al., 1997; Leone et al., 2001), Fe oxides have an important role in the sorption of IMI herbicides, and they affect their persistence in the soil. For soils which are relatively rich in Al and Fe, pH-dependent charges of the adsorbents were considered to have an additional effect on sorption of these herbicides (Wang and Liu, 1999; Gianelli et al., 2014). The surface OH groups on the Fe oxide promote deprotonating of the carboxyl, inducing a molecule-ferrihydrite interaction (Leone et al., 2001).

Weak acid herbicides such as imazethapyr and imazapic with pKa 3.9 (for both herbicides) lose a proton and are predominantly in anionic form under pH conditions near neutral, as in the range of soil pH used in this experiment (pH 5.1 - 6.1). An increase in repulsion between the molecules of these herbicides and negatively charged sites of soil colloids result in weak binding energy, and consequently, in low sorption, as checked by the magnitude of the K_f values (between 0.38 and 2.52 $mg^{1-n}\ kg^{-1}\ L^n$) and (between 0.43 and 2.72 $mg^{1-n}\ kg^{-1}\ L^n$) to imazethapyr and imazapic, respectively. Additionally, a high amount of sand in some of the soils provides slow exchange surface electrostatic which favors lower sorption. Therefore, the sorption in soils followed the order: PV > GX > CH ≈ FX > LVA > RR for imazethapyr and PV > CH > GX > LVA > RR > FX for imazapic. This sorption order in soils implied that the IMI herbicides had a different behavior for some of these soils and could have more than one type of sorption mechanism. It can be related to the strong relationship between pH values and iron oxalate content (cf. Table 2) during the sorption of IMI herbicides. These factors could have contributed, particularly, to the higher sorption among the evaluated soils samples (PV, GX and CH, with pH<5.5) for both herbicides. Particularly for imazethapyr, Ahmad and Rahman (2009) reported that to changes in soil pH beyond 5.5 would have a large effect on the retention of these herbicide. Therefore, the pH values of the LVA and FX soils (pH>5.5) may have contributed to lower sorption for both herbicides.

The $K_{f\text{-}OC}$ values found for imazethapyr and imazapic varied greatly in the different soils, ranging from 12.84 to 206.88 $mg^{1-n}\ kg^{-1}\ L^n$ and from 23.66 to 223.29 $mg^{1-n}\ kg^{-1}\ L^n$, respectively (Table 4 and 5). In accordance with these results, the OC content alone did not describe the variation found in the sorption of these herbicides; consequently, $K_{f\text{-}OC}$ could not be used to compare the relative sorption of various soils, particularly for ionizable compounds, such as imazapic and imazethapyr (Ahmad and Rahman, 2009).

Whereas none of the factors pH, oxalate iron content and OC alone explains the results obtained in the study of IMI herbicides sorption other factors can be affect too this process such as the type and percentage of clay of the soil.

Desorption of imazapic and imazethapyr

In the present study, the desorption behavior of imazapic and imazethapyr showed that the major amount of both herbicides was desorbed from the soil in the first two desorption steps, and less desorption of these herbicides occurred as the desorption steps increased. The desorbed herbicides during the first few hours were likely to have come from the most accessible sites and/or from the less-energy-release sorption mechanisms; whereas the sorbed herbicides on less accessible sites and/or more strongly adsorbed (high-energy) sites were not susceptible to desorption initially and were subsequently subject to a slow release over time (Mamy and Barriuso, 2007).

Desorption data were adjusted to the linear fitting. Figures 4 and 5 respectively show desorption curves for imazapic and imazethapyr for the evaluated soils. Table 6 shows the results for this model for both herbicides.

The molecules of both imazapic and imazethapyr showed different desorption behaviors. The CH and PV soils were found to have a low desorption percentage for both herbicides (less than 50%), and the GX soil (~50%), only for imazethapyr, that is, there was greater difficulty in releasing the herbicide into the soil solution. The occurrence of low desorption might indicate hysteresis and it could be attributed to several causes. This behavior, i.e., low desorption of IMI herbicides to these soils samples could be associated to the bonding of herbicide molecules to specific sorption sites, such as amorphous iron oxide. Pusino and

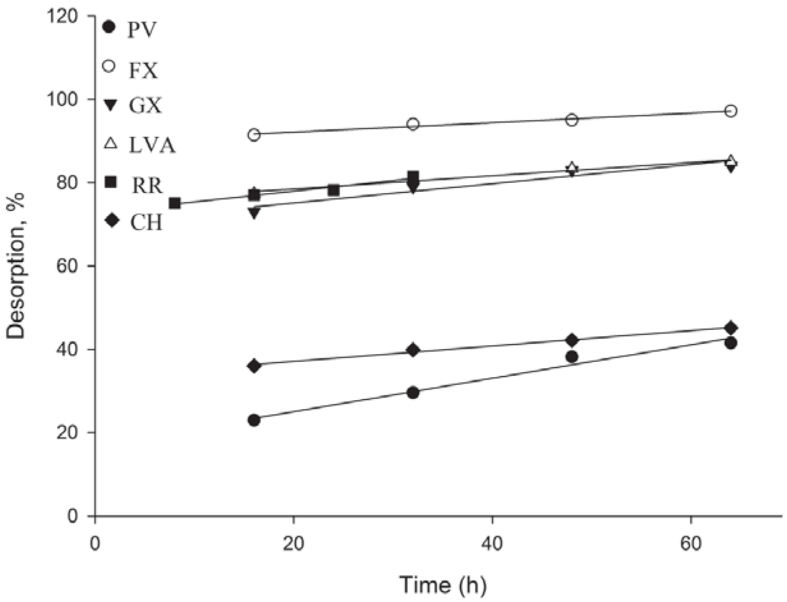

Figure 4 - Desorption percentages of imazapic in the soils in the soils LVA (Ferralsol), FX (Dystric Plinthosol), GX (Dystric Gleysol), CH (Cambisol), PV (Alisol) and RR (Regosol), at different times.

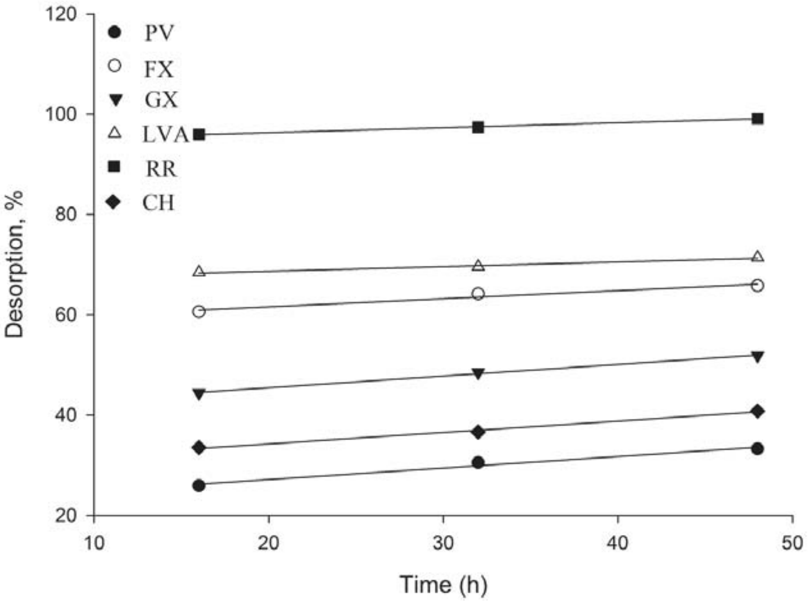

Figure 5 - Desorption percentages of imazethapyr in the soils LVA (Ferralsol), FX (Dystric Plinthosol), GX (Dystric Gleysol), CH (Cambisol), PV (Alisol) and RR (Regosol), at different times.

co-workers (Pusino et al., 1997) evaluated sorption-desorption behavior to imazapyr in six soil samples and the lowest desorption was found for two of them because of the higher amorphous iron oxide content. Imazethapyr had the same behavior as CH and GX, as previously observed; however, CH and GX show high iron oxalate content. Consequently, imazethapyr could have a carryover effect on sensitive succeeding crops in these three soils and imazapic, in the two of the evaluated soils.

In RR, LVA, FX, a higher desorption percentage was found for imazapic and imazethapyr (greater than 70%), and for the GX soil (only imazapic). It could be because of the pH of the soils, particularly for soils LVA and FX, whose pH is above 5.5 (Ahmad and Rahman, 2009). Moreover, these three soil samples present similar iron oxalate contents that may have contributed to a

Table 6 **-** Desorption data fitting the linear polynomial model to the different soil samples

Soil	Imazapic		Imazethapyr	
	a	b	a	b
GX	0.23 (±0.05)	70.50 (±2.2)	0.23 (±0.01)	40.78 (±0.46)
LVA	0.16 (±0.02)	75.29 (±0.88)	0.09 (±0.01)	66.78 (±0.43)
FX	0.11 (±0.01)	89.82 (±0.57)	0.16 (±0.03)	58.33 (± 1.20)
CH	0.19 (±0.01)	33.38 (±0.57)	0.23 (±0.02)	29.71 (±0.70)
PV	0.40 (±0.05)	17.01 (±2.0)	0.23 (±0.03)	22.51 (±1.15)
RR	0.26 (±0.04)	72.83 (±0.78)	0.10 (±0.005)	94.31 (±0.17)

LVA (Ferralsol), FX (Dystric Plinthosol), GX (Dystric Gleysol), CH (Cambisol), PV (Alisol) and RR (Regosol). Numbers in parentheses are standard errors. The coefficients of determination (R^2) were > 0.92 in all cases.

comparable level of desorption. The high desorption percentage found for these soil samples suggests a high mobility of herbicides through the soil profile, offering leaching risks, then polluting groundwater.

Furthermore, the higher desorption percentage did not match the order of the decreasing sorption of herbicides for all soils. The sorbed molecules were released into the aqueous solution in the following order: RR > LVA > FX > GX > CH > PV for imazethapyr and FX > LVA > RR > GX > CH > PV for imazapic.

Thus, these results show that multiple mechanisms are involved in the sorption–desorption of herbicides in soils, and different mechanisms could be operable for sorption as compared with the desorption processes. The understanding of these mechanisms depend not only on the sorption coefficients, but also on the manner in which each compound interacts with the adsorbent surface. In addition, the results found in this study showed that for safe use and effective performance of these IMI herbicides in agricultural crops, particularly in Clearfield® production systems, both the soils and their physicochemical properties have to be taken into consideration.

ACKNOWLEDGMENTS

The authors thank the funding agencies for financial support: CAPES, CNPq, and FAPEMIG.

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