

Soil pH on Mobility of Imazaquin in Oxisols with Positive Balance of Charges

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The influence of soil pH on the leaching potential of the ionizable herbicide imazaquin was assessed on the profile of two highly weathered soils having a net positive charge in the B horizon, in contrast to a soil having a net negative charge in the whole profile, using packed soil column experiments. Imazaquin leached to a large extent and faster at K_d values lower than 1.0 L kg^{-1} , a much more lenient limit than usually proposed for pesticides in the literature ($K_d < 5.0 \text{ L kg}^{-1}$). The amount of imazaquin leached increased with soil pH. As the soil pH increased, the percentage of imazaquin in the anionic forms, the negative surface potential of the soils, as well as imazaquin water solubility also increased, thus reducing sorption because of repulsive electrostatic forces (hydrophilic interactions). For all surface samples (0–0.2 m), imazaquin did not leach at soil pH values lower than pK_a (3.8) and more than 80% of the applied amount was leached at pH values higher than 5.5. For subsurface samples from the acric soils, imazaquin only began to leach at soil pH values > zero point of salt effects (ZPSE > 5.7). In conclusion, the use of surface K_{oc} values to predict the amount of imazaquin leached within soil profiles having a positive balance of charges may greatly overestimate its actual leaching potential.

KEYWORDS: Leaching; sorption; imidazolinone; soil surface potential; charge

INTRODUCTION

In the last 20 years, imidazolinone herbicides have been developed. They act by inhibiting the action of a key plant enzyme (acetolactate synthase, ALS), stopping plant growth, and eventually causing plant death. These compounds are reported to have very low toxicity to animals (1), although having a wide range of toxicity to nontarget plants (2). Because of their low application rates (ALS-inhibiting herbicides are characterized by low application rates) and low overall use amounts, imidazolinone concentrations are expected to be low in most water resources despite their high leaching potential. In fact, their analytical detections in water collected from environmental settings in the United States have been rare, and the few reported detections have been at very low concentrations ($\eta\text{g L}^{-1}$). However, in 1998, imazaquin was found above the method-reporting limit ($10 \eta\text{g L}^{-1}$) in 32% of the water samples collected from midwestern streams and rivers of the United States (3).

Imazaquin [2-(4-isopropyl-4-methyl-5-oxo-4,5-dihydroimidazol-1H-2-yl)-3-quinoline-3-carboxylic acid] is a imidazolinone herbicide commonly used in Brazil in association to soybean crops to control a wide range of broadleaf weeds when applied post- or pre-emergence or is preplant-incorporated. Imazaquin is an amphoteric molecule with both acid carboxyl ($pK_a = 3.8$) and basic quinoline ($pK_a = 1.8$) groups, which ionize depending on soil pH values. It is moderately water-soluble (60 mg L^{-1} , in distilled water at $25 \text{ }^\circ\text{C}$), has a low vapor pressure ($< 2.66 \times 10^{-6} \text{ Pa}$ at $45 \text{ }^\circ\text{C}$), and presents low to moderate sorption ($K_{oc} = 0.4\text{--}2.2$ and $K_d = 0.2\text{--}8.8 \text{ mL g}^{-1}$) (4, 5). Its sorption is positively related to the organic carbon (OC) content and negatively related to pH in most soils with permanent negative charges (6–10). Nonetheless, many other soil attributes such as ionic strength, electric surface potential, clay, exchangeable Al, extractable P, and Fe, Al, and Mn oxide contents may also affect its sorption as well as its mobility in soils (7, 11–13). Imazaquin sorbs to soils mainly because of hydrophobic interactions but other mechanisms, such as electrostatic forces (hydrophilic interactions), may dictate sorption on highly weathered soils, rich in Fe oxides (7). In a recent study, working with a sulfonylurea herbicide (proprifluron), a weakly acid molecule as well, the authors observed that trends in anion sorption correlated well to the ratio of anion-exchange capacity

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(AEC) to cation-exchange capacity (CEC) and hence concluded that electrostatic forces were the primary sorption mechanism involved in it (14). They also pointed out that negatively charged sites (CEC) block the access of organic anion to positively charged sites (AEC) on the soil surface.

Imazaquin exists mostly in the anionic form at a soil pH range suitable for agriculture (pH 5.0–7.0) and therefore is repelled by the anionic sites that are predominant in the upper soil layer, mainly because of the presence of organic matter (11, 15). It explains the low sorption potential usually encountered for weakly acidic herbicides (16). These herbicides are reported to be much more mobile in soils than weakly basic and nonionizable herbicides (5). For example, imazaquin was found to be much more mobile than atrazine (17), metribuzin (17), prometryn (6), cinmethylin (6), and metolachlor (5).

The relatively long persistence (18–20) and the low sorption (7, 15) of imazaquin endorse its potential for mobility, although it is applied at low rates (150 g ai ha⁻¹). Consequently, imazaquin does have the potential to leach beyond the active root zone and enter ground or surface water systems. In Brazil, groundwater contamination by the use of such pesticides has risen concerns during the recent years as a consequence of their increased use as well as their mobility potential.

In certain areas of intensive soybean cropping in the northern part of São Paulo, Brazil, more than 170 000 ha of soil with acric properties were identified. These acric soils comprehend the end point of the weathering scale and can have a positive balance of charges in the B horizon because of low organic matter and high Fe₂O₃ and Al₂O₃ contents resulted from intense desilication (21). In most soils, anionic molecules may leach to groundwater, but it may not be the case for acric soils because of electrostatic attractive forces (or hydrophilic interactions). Therefore, it is crucial to understand the effects of soil pH on mobility of imazaquin in soils with variable charges, such as the acric soils. Soil mobility is an important process that dictates pesticide availability, bioactivity, as well as water quality. Furthermore, transport rates help to predict environmental fate and risks associated to the use of a specific pesticide.

The aim of this research was to evaluate the effects of soil pH variations on the mobility of imazaquin in the surface and subsurface layers of two acric oxisols, having a positive balance of charges in the B horizon, in contrast to a nonacric Alfisol, using packed soil columns with disturbed soil samples. This method was adopted to supplement our previous batch sorption work (12), thus providing breakthrough curves and soil profile distribution for imazaquin. Although the column leaching method does not quantitatively predict leaching behavior under field conditions, the results may assist better in deciding whether additional semifield or field testing has to be carried out for substances showing a high mobility potential in laboratory tests (22), as is the case for imazaquin.

MATERIAL AND METHODS

Soils. Soil samples from surface and subsurface layers from a sand clayey Anionic Acrudox (SCAA), a clayey Anionic Acrudox (CAA), and a clayey Rhodic Kandudalf (CRK) were collected at the northern region of São Paulo state (latitudes at 20 and 22° S and longitudes at 47 and 49° W), Brazil. The surface samples were collected from 0.0 to 0.2 m, whereas the subsurface samples were collected from 1.0 to 1.3 m for the SCAA, 1.0 to 1.4 m for the CAA, and 0.8 to 1.0 m for the CRK. These depths represented the best expression of the B horizon for each soil.

OC was obtained after oxidation of the soil organic matter with a potassium dichromium solution in the presence of sulfuric acid, and the excess of dichromium was titrated with sulfate ferrous ammoniacal

[Fe(NH₄)₂(SO₄)₂·6H₂O] (23). Fe and Al oxides were obtained after the addition of 9 mol L⁻¹ H₂SO₄. Amounts of gibbsite and kaolinite were quantified in the clay fraction by thermo differential analysis (TDA) (24, 25), after removal of Fe oxides and organic matter. Particle size analysis was performed according to the densimeter method (26). Specific surface (SS) was quantified by the EMEG method (27), by drying the soil (110 °C, 24 h) instead of using P₂O₅ (28). Soil pH was determined in 0.01 mol L⁻¹ CaCl₂, using a 1:2.5 soil-solution ratio. Zero point of salt effect (ZPSE) was obtained by the titration method, using three concentrations of KCl (0.1, 0.01, and 0.001 mol L⁻¹). The electric surface potential (Ψ_0) was calculated by the Nernst equation [$\Psi_0 = 59.1(\text{ZPSE} - \text{pH})$] (29). The permanent (σ_0) and variable (σ_{var}) densities of charge were quantified based upon the selectivity of cesium (Cs⁺) into the siloxane cavities of the 2:1 clay minerals, rather than in the ionizable surfaces (30).

Soils Incubation (pH Adjustments). Soil samples (4 kg) were incubated with either CaCO₃ p.a. or 1 mol L⁻¹ HCl to obtain pH values in the range between 3 and 8 (31, 32). During the incubation period (about 90 days), soil moisture contents were kept constant (30%, air-dried). Later, soil samples were air-dried, sieved (2 mm), and stored in plastic bags.

Leaching Experiments. A completely randomized 3 (soils) × 4 (soil pH values) factorial design was adopted. Treatments were established to evaluate the influence of soil pH on imazaquin mobility in the soils, using packed soil columns as the experimental unit. Glass columns (40 cm in length and 5 cm in diameter), having a conical end at the bottom, were used for soil packing. Glass wool and sterilized sand (washed with HCl) were used as a support, and then soil samples were evenly added to columns (up to 30 cm). Glass wool was also placed on top to promote an even dispersion of water. Packed soil bulk density and porosity were calculated on the basis of the column volume (589 cm³).

In all treatments (in triplicate), soil samples were water-saturated by capillary forces and water excess was percolated for about 2 h. Soil columns were placed in a dark room with a temperature control (25 ± 2 °C), and rainfall was simulated at a constant water flow (2.44 mm h⁻¹, totaling about 350 mm in 6 days) with the aid of a peristaltic pump. Imazaquin was applied at its maximum recommended field rate (150 g a.i. ha⁻¹), in a short pulse, from a solution prepared with ¹⁴C-imazaquin (¹⁴C-COOH, specific activity = 0.80 MBq mg⁻¹, and purity = 98%), diluted in 20% methanol.

Column leachates were collected at 12 h intervals for a total of 6 days. At each interval, two replicates (10 mL) were taken and added to 10 mL of scintillation solution (Insta-Gel XF) to measure leachate radioactive concentration by a liquid scintillation counter (LSC). To determine the identity of the radioactivity, thin-layer chromatography (TLC) was performed with the remaining leachate, after concentration on a rotary evaporator at 45 °C. The solvent system used with the TLC plate (Al, Silicagel 60 F₂₅₄) was dichloromethane/acetic acid (95:5, v/v). Analytical-grade imazaquin was used as a standard. A radioscaner was used to detect radioactive compounds on TLC plates. For all treatments, the total radioactivity corresponded to original imazaquin (data not shown).

After leaching completion, pressurized air was used to remove soil samples from the columns. During this procedure, soil columns were sectioned into 5 cm layers. Afterward, soil samples were air-dried and pulverized, and triplicate subsamples (0.4 g, air-dried) were taken to detect residual radioactivity in the soil layers by combustion in a biological oxidizer.

The average radioactive recovery, i.e., amounts leached plus that bound to soils, was equal to 100.6 ± 7.6% across all treatments. Considering the recalcitrance of imazaquin, this overall high recovery may suggest that losses because of either volatilization or degradation were minimal. All data were normalized, so that recovery would be equal to 100%. The normalization resulted in lower values for the mean standard deviation.

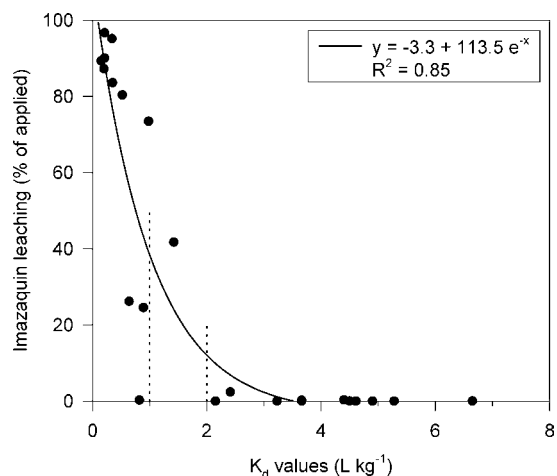
RESULTS AND DISCUSSION

Soil Properties. The SCAA presented lighter texture and lower specific surface (SS), organic carbon (OC), SiO₂, Fe₂O₃,

Table 1. Physical, Electrochemical, Chemical, and Mineralogical Attributes of the Soils

soils ^a	layer (m)	sand (g kg ⁻¹)	silt (g kg ⁻¹)	clay (g kg ⁻¹)	WDC (g kg ⁻¹)	SS (m ² g ⁻¹)	ZPSE	σ_0 (mmol kg ⁻¹)	σ_{var} (mmol kg ⁻¹)	σ_{var}/σ_0	OC (g kg ⁻¹)	SiO ₂ (g kg ⁻¹)	Fe ₂ O ₃ (g kg ⁻¹)	Al ₂ O ₃ (g kg ⁻¹)	Kt (g kg ⁻¹ of clay ^b)	Gb (g kg ⁻¹ of clay ^b)
SCAA	0.0–0.2	610	40	350	180	64.7	3.4	8.4	32.3	3.8	16	52	59	113	248	200
	1.0–1.3	510	40	450	0	53.2	6.1	1.3	18.4	14.2	6	80	134	172	196	189
CAA	0.0–0.2	170	230	600	340	64.7	3.6	8.2	39.9	4.9	20	112	321	248	172	375
	1.0–1.4	130	230	640	20	75.5	5.7	4.7	16.1	3.4	5	114	338	257	216	431
CRK	0.0–0.2	60	120	820	420	134.1	3.7	30.2	63.1	2.1	26	153	298	183	249	59
	0.8–1.0	80	220	700	90	151.3	3.6	30.9	35.4	1.2	7	227	273	237	263	80

^a SCAA, sand clayey Anionic Acrudox; CAA, clayey Anionic Acrudox; CRK, clayey Rhodic Kandudalf; WDC, water dispersible clay; SS, specific surface; ZPSE, zero point of salt effect; σ_0 , permanent charge; σ_{var} , variable charge; σ_{var}/σ_0 , ratio between variable and permanent charge; OC, organic carbon; SiO₂, Si oxide; Fe₂O₃, Fe oxide; Al₂O₃, Al oxide; Kt, kaolinite; Gb, gibbsite. ^b Deferrified clay.

**Figure 1.** Correlation between imazaquin leaching and its sorption coefficients (K_d values).

and Al₂O₃ contents, whereas the CRK presented heavier texture and higher SS, OC, SiO₂, and Al₂O₃ contents (Table 1). The ratios between variable and permanent charge densities higher than 1.0 highlighted the predominance of variable charges for all soils but mainly for the acric soils. The nature of these charges is related to Al₂O₃ and Fe₂O₃ resulting from the intense process of desilication occurring in tropical soils. For all soils, the ZPSE values were relatively low for the surface layers because of the presence of organic matter; however, these values were much higher for the subsurface layers of the acric soils (Table 1), as a result of the fewer permanently charged sites, lower organic matter, and higher Fe₂O₃ and Al₂O₃ contents (33).

Batch Sorption versus Column Leaching. In previous research (12), imazaquin sorption potential was measured for the same soils and conditions (or same soil pH values), and it was observed that K_d values were negatively related to pH and positively related to electric surface potential (Ψ_0) of the soils. Both soil attributes affected water solubility and electrostatic interactions between imazaquin and the soil colloids. In this study, imazaquin leaching potential was closely related to its sorption ($R^2 = 0.84$, Figure 1). Therefore, pH and Ψ_0 should also be affecting imazaquin leaching potential.

Imazaquin was found in the leachate only at K_d values lower than 2.0 L kg⁻¹. In general, more than 70% of the applied amount leached entirely through the columns when K_d values were lower than 1.0 L kg⁻¹ (Figure 1). However, there were some discrepant points in the curve. It reinforced the limitations of using batch equilibrium data (K_d values) alone to predict leaching potential of anionic organic molecules in highly weathered soils, mainly in those with a positive balance of

Table 2. Soil and Molecule Charges and Packing on Leaching and Sorption of Imazaquin at Different Soil pH Values

pH	Ψ_0 (mV)	ϕ_a (%)	porosity (%)	water velocity (mm h ⁻¹)	total leached (% applied)	K_d (L kg ⁻¹) (Rocha et al., 2002)
SCAA ^a (0.0–0.2 m)						
3.2	+12	20.1	47.6	5.0	<0.1	3.7
4.4	-59	79.9	50.1		73.4	1.0
5.6	-130	98.4	48.8		83.6	0.4
7.0	-213	99.9	49.2		89.3	0.2
SCAA (1.0–1.3 m)						
3.2	+171	20.1	45.6	5.2	0.3	4.4
4.2	+112	71.5	46.4		0.3	3.7
5.9	+12	99.2	48.5		0.3	0.8
7.6	-89	100.0	47.2		96.7	0.2
CAA (0.0–0.2 m)						
3.4	+12	28.5	48.5	4.9	0.1	3.2
4.3	-41	76.0	50.7		41.7	1.4
5.5	-112	98.0	49.8		80.4	0.5
7.4	-225	100.0	50.9		90.1	0.2
CAA (1.0–1.4 m)						
3.3	+142	24.0	50.2	4.8	<0.1	4.5
5.0	+41	94.1	52.1		<0.1	2.2
6.7	-59	99.9	51.4		95.1	0.3
CRK (0.0–0.2 m)						
3.2	+30	20.1	55.7	4.4	<0.1	6.7
4.2	-30	71.5	55.4		<0.1	5.3
5.1	-83	95.2	56.1		2.4	2.4
6.8	-183	99.9	55.4		26.2	0.6
CRK (0.8–1.0 m)						
3.2	+24	20.1	54.6	4.5	<0.1	4.9
4.2	-35	71.5	54.6		<0.1	4.6
5.8	-130	99.0	55.3		24.5	0.9
7.6	-236	100.0	54.8		87.2	0.2

^a SCAA, sand clayey Anionic Acrudox; CAA, clayey Anionic Acrudox; CRK, clayey Rhodic Kandudalf; Ψ_0 , electric surface potential; ϕ_a , anionic species of imazaquin, $(1 - \phi_n) \times 100$, where ϕ_n , neutral species of imazaquin, $(1 + 10^{\text{pH} - \text{pK}_a})^{-1}$; water velocity, flow/porosity; K_d , partition coefficient.

charges (34). The authors observed that, in general, K_d values overestimated imazaquin leaching potential in a heavy-textured acric soil.

For all soils, the amount of imazaquin leached increased with soil pH (Table 2). As pH increased, imazaquin water solubility also increased (11), thus reducing its sorption potential because of hydrophobic partition to the soil organic matter. Using FTIR and EPR spectroscopy, weak interactions were observed between imazaquin and a Brazilian oxisol and its humic acid (35). The authors pointed out that the hydrophobic interaction was the main mechanism involved in the sorption of imazaquin, and they ruled out the possibility of imazaquin forming ligand

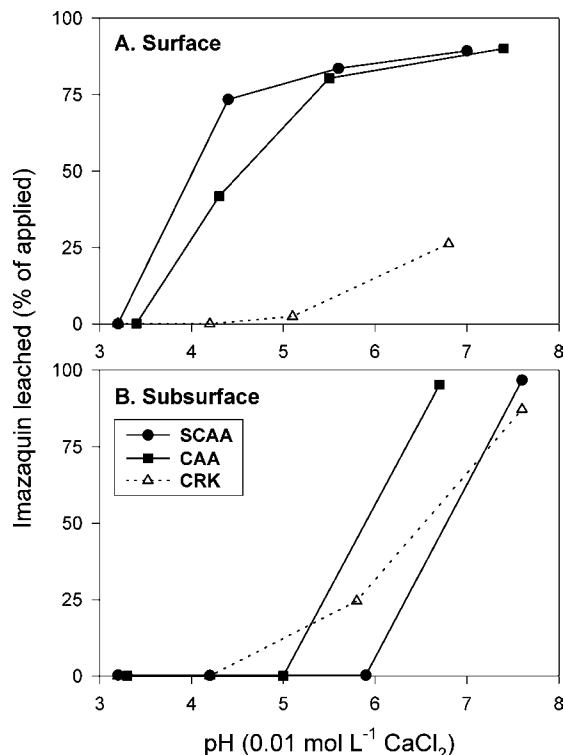


Figure 2. Imazaquin leached at different soil pH values from the surface and subsurface layers. SCAA, sand clayey Anionic Acrudox; CAA, clayey Anionic Acrudox; and CRK, clayey Rhodic Kandiudalf.

exchange (charge transfer) with the humic acid fraction. Nevertheless, organic acids would form ligand exchange with oxide structural moieties, such as OH^- and OH_2 , at low pH values (36).

Likewise, the percentage of imazaquin molecules in the anionic form (ϕ_a) increased with soil pH, as well as the negative electric surface potential of the soils (Ψ_0) (Table 2), thus reducing sorption because of repulsive electrostatic forces (8, 12). Other authors noticed that hydrophilic interactions controlled by anion-exchange processes were crucial for estimating sorption of weakly acidic molecules in variable-charge soils (14, 37). Therefore, both molecule properties and soil parameters should enhance imazaquin leaching potential at high soil pH values.

Surface Layers Leaching. In the surface layers, imazaquin did not leach completely through the columns at pH values lower than $\text{p}K_a$ (Figure 2A and Table 2). At these low soil pH values (<3.8), most imazaquin molecules were in the neutral forms; consequently, its water solubility was reduced and its sorption was enhanced because of hydrophobic partitioning. Moreover, the high proton concentration (pH values either close or lower than ZPSE) may have assured protonation of most soil functional groups, mainly those of soil organic matter most abundant in the surface layer, favoring other sorption mechanisms because imazaquin may also sorb as a result of proton transfer and hydrogen bonding at soil pH values near 3.0 (35).

Imazaquin began to leach at pH values higher than 4.2 for the surface layers of the acric soils. At soil pH values higher than 5.5, more than 80% of the applied imazaquin was leached (Figure 2A and Table 2). At these soil pH values, more than 98% of the imazaquin molecules were in the negative form and the soils were also negatively charged (Ψ_0 , Table 2). It probably has negatively affected sorption because of repulsive electrostatic forces (hydrophilic interactions). Moreover, hydrophobic interactions were also negatively affected once solubility of imaza-

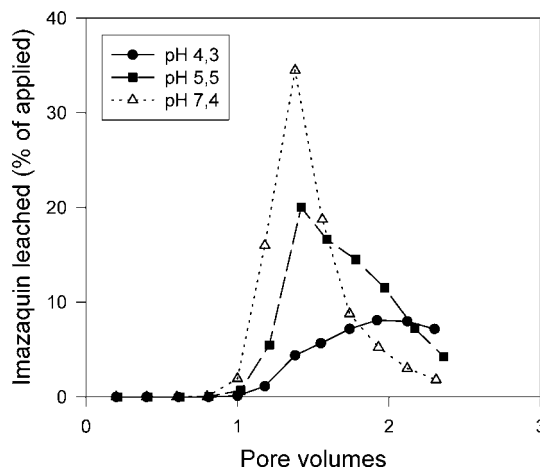


Figure 3. Breakthrough curves for imazaquin at different soil pH values in the surface layer of the CAA. CAA, clayey Anionic Acrudox.

quin increased with soil pH (11). It was already observed that the lower the Ψ_0 (more negative), the lower the sorption of imazaquin because of repulsive electrostatic forces (12). Both of these mechanisms should enhance imazaquin leaching potential in soils.

The amount of imazaquin leached from the surface layer of the CRK was much lower than that from the acric soils, mainly at pH values higher than 4.2 (Figure 2A). Even at high soil pH values, the amount of imazaquin leached from this soil never exceeded 26.2% of the applied amount (Figure 2A and Table 2). The higher OC, SS, and clay contents of this soil (Table 1) should be favoring chemical sorption, besides favoring physical sorption of imazaquin because of diffusion and soil entrapment. Anion-exchange, hydrogen-bonding, and charge-transfer mechanisms have been shown to be significant for sorption of weakly acidic herbicides by Al and Fe oxides, clay minerals, humic acid, and anion-exchange resins (14). In addition, the higher contents of water dispersible clays (WDCs) in this soil (Table 1) may be clogging the porous soil, disrupting imazaquin preferential flow. It was previously proposed that soil water phases may be regarded as partly mobile and partly stagnant (38). The authors emphasized that solutes (such as pesticides) move by convection and dispersion in the mobile water phase and move in to and out of the stagnant regions by diffusion. Probably, the stagnant water phase should be more abundant in this soil because of its higher total clay and WDC contents (Table 1).

Subsurface Layers Leaching. Imazaquin leaching trends in the subsurface layers of the acric soils emphasized the importance of Ψ_0 on the mobility of ionizable organic molecules, such as imazaquin (Figure 2B). Imazaquin leached from these soils only at higher pH values, i.e., when pH was higher than the ZPSE (>6.1 and 5.7 for the SCAA and CAA, respectively). At $\text{p}K_a < \text{pH} < \text{ZPSE}$, the Ψ_0 became mostly positive (Table 2) and it may have enhanced sorption because of electrostatic forces, once the majority of imazaquin molecules were in the anionic forms. At this pH range, imazaquin did not leach through the subsurface layer but leached through the surface layer of the acric soils (parts A and B of Figure 2). Thus, electrostatic interactions may lessen imazaquin potential to contaminate groundwater in agricultural areas with soils having a positive balance of charges. It would be the case for highly weathered tropical soils having high Fe and Al oxide and kaolinite contents (17) but not for temperate soils or soils with 2:1 clay mineralogy. In permanently charged soils, Ψ_0 will not change to a large

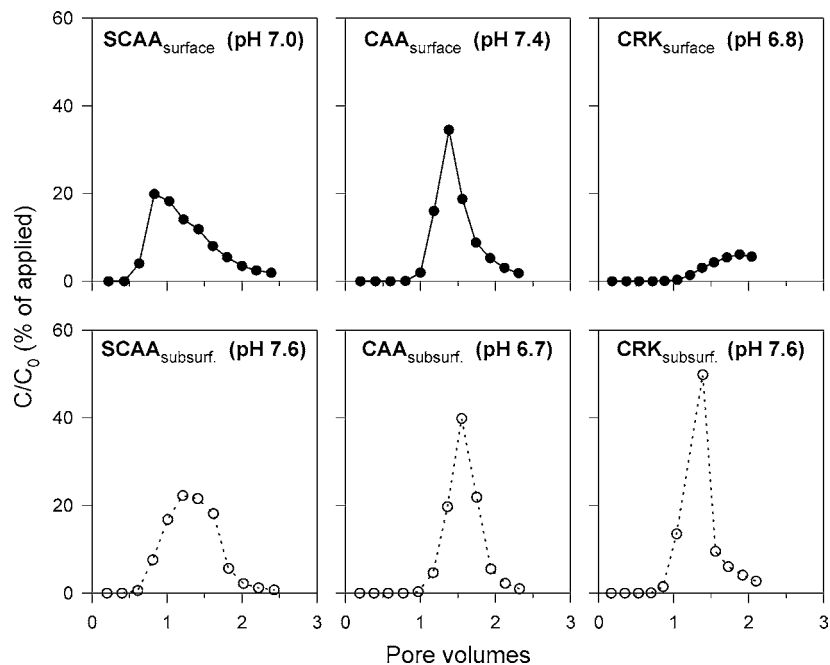


Figure 4. Breakthroughs curves for imazaquin at high pH values in the surface and subsurface layers of the soils. SCAA, sand clayey Anionic Acrudox; CAA, clayey Anionic Acrudox; and CRK, clayey Rhodic Kandiudalf.

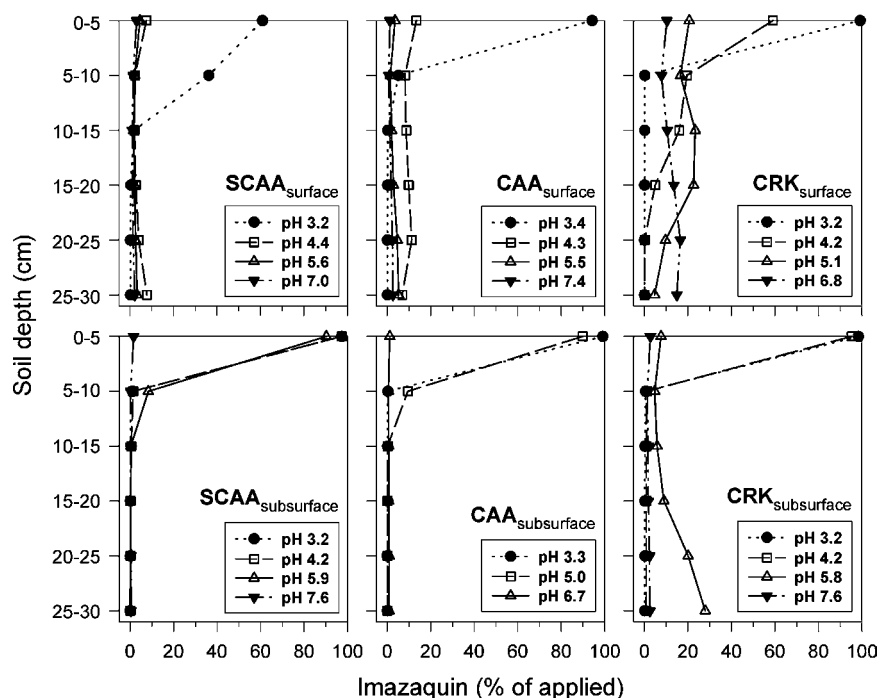


Figure 5. Imazaquin mobility at different soil pH values within the surface and subsurface layers of the soils. SCAA, sand clayey Anionic Acrudox; CAA, clayey Anionic Acrudox; and CRK, clayey Rhodic Kandiudalf.

extent with variations in hydrogen activity and, consequently, imazaquin mobility will tend to be higher. It is well-known that weakly acidic organic molecules are repelled by 2:1 clay minerals when their surface is in excess of negative charges (39–41).

Breakthrough Curves (BTCs). The shape and eluting peak of the BTCs showed that interactions between imazaquin and soils were affected by soil pH values (Figure 3). Only the surface layer of the CAA was shown as an example of overall soil behaviors. The peaks shifted to the left at higher soil pH values, meaning that imazaquin leached earlier (faster), because soil porosity was nearly the same for all treatments (Table 2). This faster leaching was likely due to the lower bind strength

between imazaquin and soil colloids at higher soil pH values (42). Furthermore, imazaquin BTCs became sharper (with reduced tailing) at higher pH values, behaving more or less like a tracer (Figure 3). The peak sharpness and the relative symmetry of the BTCs at high soil pH values implied equilibrium conditions and fast release of imazaquin (43). This behavior most likely resulted from both repulsion among electrostatic forces (hydrophilic interactions) and changes in water solubility of imazaquin (hydrophobic interactions), although it is not clear at this point which one is the primary sorption mechanism involved.

At relatively high soil pH values, imazaquin started to leach much earlier from the sandy soil (pv ~ 0.5 for the SCAA) than

from the clayey soils ($p_v \sim 1.0$ for the CAA and CRK) and the peaks were broadened for the sandy soil (Figure 4). It showed either the preferential flow of imazaquin in this coarse-textured soil or the lower affinity of imazaquin for the sand particles or both. At these high soil pH values, the transport rate of imazaquin was very fast because about 2.5 pore volumes were enough to leach more than 87% of the applied imazaquin, except for the surface layer of the CRK.

Mobility within the Profile. As expected, imazaquin distribution within the soil profile was also affected by soil pH. Almost 100% of the molecules remained in the first 10 cm layer at low pH values, i.e., at pH values lower than the ZPSE (Figure 5), reinforcing the importance of electrostatic interactions to properly predict imazaquin mobility within the profile of soils having pH-dependent charges. At higher pH values ($>ZPSE$), however, the molecules were more or less uniformly distributed in the profile of the soil columns. Under these pH conditions, imazaquin may tend to be entirely leached if enough water was applied to the system. Nevertheless, the subsurface layer of the CRK still had a great majority of the molecules in the first 10 cm layer at soil pH values equal to 4.2 (higher than ZPSE). It probably happened because of the nearness of pH to ZPSE and to the high SS, clay, and iron oxide contents of this soil.

Imazaquin will tend to leach in soils with K_d values lower than 2.0 L kg^{-1} , but it will be more problematic in soils with K_d values lower than 1.0 L kg^{-1} . Imazaquin does have the potential to leach through the surface layers of the acric soils at natural soil pH values. If liming is performed on the surface layer of these acidic soils, the overall leaching potential should be even higher because imazaquin mobility increases with soil pH. However, once it reaches the subsurface layers, imazaquin will only move downward at extremely high pH values for tropical soils, i.e., at pH values either close or above neutrality. The presence or predominance of anion-exchange sites in the subsurface layers of acric soils at natural soil pH values (lower than ZPSE values) will lessen imazaquin leaching potential. Consequently, the use of surface K_{oc} values to predict imazaquin leaching potential in acric soils will likely overestimate its actual mobility in the whole soil profile. In summary, imazaquin will not tend to leach beyond the subsurface layers of acric soils, minimizing the possibility to contaminate groundwater resources.

LITERATURE CITED

- Meister, R. T. *Farm Chemicals Handbook '97*; Meister Publishing Company: Willoughby, OH, 1997.
- Peterson, H. G.; Boutin, C.; Martin, P. A.; Freemark, K. E.; Ruecker, N. J.; Moody, M. J. Aquatic phyto-toxicity of 23 pesticides applied at expected environmental concentrations. *Aquat. Toxicol.* **1994**, *28*, 275–292.
- Battaglin, W. A.; Furlong, E. T.; Burkhardt, M. R.; Peter, C. J. Occurrence of sulfonylurea, sulfonamide, imidazolinone, and other herbicides in rivers, reservoirs, and ground water in the Midwestern United States, 1998. *Sci. Total Environ.* **2000**, *248*, 123–133.
- Roberts, T.; Hutson, D. H.; Lee, P. W.; Nicholls, P. H.; Plimmer, J. R. *Metabolic Pathways of Agrochemicals. Part 1: Herbicide and Plant Regulators*. The Royal Chemistry Society: Cambridge, U.K., 1998.
- Weber, J. B.; Mckinnon, E. J.; Swain, L. R. Sorption and mobility of ^{14}C -labeled imazaquin and metolachlor in four soils as influenced by soil properties. *J. Agric. Food Chem.* **2003**, *51*, 5752–5759.
- Liu, S. L.; Weber, J. B. Retention and mobility of AC 252,214 (imazaquin), chlorsulfuron, prometryn, and SD 95481 (cinmethylin) in soils. *Proc. South Weed Sci. Soc.* **1985**, *38*, 465–474.
- Regitano, J. B.; Bischoff, M.; Lee, L. S.; Reichert, J. M.; Turco, R. F. Retention of imazaquin in soil. *Environ. Toxicol. Chem.* **1997**, *16*, 397–404.
- Regitano, J. B.; Alleoni, L. R. F.; Vidal-Torrado, P.; Casagrande, J. C.; Tornisielo, V. L. Imazaquin sorption in highly weathered tropical soils. *J. Environ. Qual.* **2000**, *29*, 894–900.
- Bresnahan, G. A.; Koskinen, W. C.; Dexter, A. G.; Lueschen, W. E. Influence of soil pH—sorption interactions on imazethapyr carry-over. *J. Agric. Food Chem.* **2000**, *48*, 1929–1934.
- Li, K.; Liu, W.; Xu, D.; Lee, S. Influence of organic matter and pH on bentazone sorption in soils. *J. Agric. Food Chem.* **2003**, *51*, 5362–5366.
- Stougaard, R. N.; Shea, P. J.; Martin, A. R. Effect of soil type and pH on adsorption, mobility, and efficacy of imazaquin and imazethapyr. *Weed Sci.* **1990**, *38*, 67–73.
- Rocha, W. S. D.; Regitano, J. B.; Alleoni, L. R. F.; Tornisielo, V. L. Sorption of imazaquin in soils with positive balance of charges. *Chemosphere* **2002**, *49*, 263–270.
- Vasudevan, D.; Cooper, E. M. 2,4-D sorption in iron oxide-rich soils: Role of soils phosphate and exchangeable Al. *Environ. Sci. Technol.* **2004**, *38*, 163–170.
- Hyun, S.; Lee, L. S. Factors controlling sorption of prosulfuron by variable-charge soils and model sorbents. *J. Environ. Qual.* **2004**, *33*, 1354–1361.
- Loux, M. M.; Liebl, R. A.; Slife, F. W. Adsorption of imazaquin and imazethapyr on soils, sediments, and selected adsorbents. *Weed Sci.* **1989**, *37*, 712–718.
- Koskinen, W. C.; Harper, S. S. The retention process: Mechanisms. In *Pesticides in the Soil Environment: Process, Impacts, and Modeling*, 2nd ed.; Cheng, H. H., Ed.; SSSA: Madison, WI, 1990; pp 51–77.
- Goetz, A. J.; Wehtje, G.; Walker, R. H.; Hajek, B. Soil solution and mobility characterization of imazaquin. *Weed Sci.* **1986**, *34*, 788–793.
- Basham, G. W.; Lavy, T. L. Microbial and photolytic dissipation of imazaquin in soil. *Weed Sci.* **1987**, *35*, 865–870.
- Cantwell, J. R.; Liebl, R. A.; Slife, F. W. Biodegradation characteristics of imazaquin and imazethapyr. *Weed Sci.* **1989**, *37*, 815–819.
- Loux, M. M.; Liebl, R. A.; Slife, F. W. Availability and persistence of imazaquin, imazethapyr, and clomazone in soils. *Weed Sci.* **1989**, *37*, 259–267.
- Alleoni, L. R. F.; Camargo, O. A. Potencial eléctrico superficial e carga eléctrica líquida de latossolos ácidos. *Rev. Bras. Cienc. Solo* **1994**, *18*, 181–185.
- OECD 312. Guidelines for the testing of chemicals: Leaching in soil columns, 2004; p 15.
- Nelson, D. W.; Sommers, L. E. Total carbon, organic carbon, and organic matter. In *Methods of Soil Analysis. Part 3. Chemical Methods*; Sparks, D. L., Ed.; SSSA: Madison, WI, 1996; pp 961–1010.
- Warshaw, C. M.; Roy, R. Classification and scheme for the identification of layer silicates. *Geol. Soc. Am. Bull.* **1961**, *72*, 1455–1492.
- Jackson, M. L. Soil chemical analysis. Advanced course. ASA, Madison, WI, 1969.
- Gee, G. W.; Or, D. Particle-size analysis. In *Methods of Soil Analysis. Part 4. Physical Methods*; Dane, J. H., Topp, G. C., Eds.; SSSA: Madison, WI, 2002; pp 255–294.
- Cihacek, L. J.; Bremner, J. M. A simplified ethylene glycol monoethyl ether procedure for assessment of soil surface area. *Soil Sci. Soc. Am. J.* **1979**, *43*, 821–822.
- Ratner-Zohar, Y.; Banin, A.; Chen, Y. Oven drying as a pretreatment for surface-area determinations of soils and clays. *Soil Sci. Soc. Am. J.* **1983**, *47*, 1056–1058.

- (29) Singh, U.; Uehara, G. Electrochemistry of the double layer: Principles and applications in soils. In *Soil Physical Chemistry*; Sparks, D. L., Ed.; CRC Press: Boca Raton, FL, 1999; pp 1–46.
- (30) Anderson, S. J.; Sposito, G. Cesium-adsorption method for measuring accessible structural surface charge. *Soil Sci. Soc. Am. J.* **1991**, *55*, 1569–1576.
- (31) Barrow, N. J. A mechanistic model for describing the sorption of phosphate by soils. *J. Soil Sci.* **1983**, *34*, 733–750.
- (32) Barrow, N. J. Modeling the effects of pH on phosphate sorption by soils. *J. Soil Sci.* **1984**, *35*, 283–297.
- (33) Camargo, O. A.; Alleoni, L. R. F. Zero point of salt effect of acric soils. In *World Congress of Soil Science*. Montpellier, France, 1998; compact disk.
- (34) Regitano, J. B.; Prata, F.; Rocha, W. S. D.; Tornisielo, V. L.; Lavorenti, A. Imazaquin mobility in tropical soils in relation to soils moisture and rainfall timing. *Weed Res.* **2002**, *42*, 271–279.
- (35) Ferreira, J.; Martin-Neto, L.; Vaz, C. M. P.; Regitano, J. B. Mechanisms of imazaquin sorption to a humic acid extracted from a typical Brazilian Oxisol. *J. Environ. Qual.* **2002**, *31*, 1665–1670.
- (36) Evanko, C. R.; Dzombak, D. A. Influence of structural features on sorption of NOM-analogue organic acids to goethite. *Environ. Sci. Technol.* **1998**, *32*, 2846–2855.
- (37) Hyun, S.; Lee, L. S.; Rao, P. S. C. Significance of anion exchange in pentachlorophenol sorption by variable-charge soils. *J. Environ. Qual.* **2003**, *32*, 966–976.
- (38) van Genuchten, M. T.; Wierenga, P. J. Mass transfer studies in sorbing porous media. *Soil Sci. Soc. Am. Proc.* **1976**, *40*, 473–480.
- (39) Borggaard, O. K.; Streibig, J. C. Chlorsulfuron adsorption by humic acid, iron oxide, and montmorillonite. *Weed Sci.* **1988**, *36*, 530–534.
- (40) Celis, R.; Hermosin, M. C.; Cox, L.; Cornejo, J. Sorption of 2,4-dichlorophenoxyacetic acid by model particles simulating natural occurring soil colloids. *Environ. Sci. Technol.* **1999**, *33*, 1200–1206.
- (41) Leone, P.; Nègre, M.; Gennari, M.; Boero, V.; Celis, R.; Cornejo, J. Adsorption of imidazolinone herbicides on smectite–humic acid and smectite–ferrihydrite associations. *J. Agric. Food Chem.* **2002**, *50*, 291–298.
- (42) Baughman, T. A.; Shaw, D. R. Effect of wetting/drying cycles on dissipation patterns of bioavailable imazaquin. *Weed Sci.* **1996**, *44*, 380–382.
- (43) Selim, H. M.; McGrowen, S. L.; Johnson, R. M.; Pepperman, A. B. Fate of metribuzin from alginate controlled release formulations in a sharkey soil: 2. Transport. *Soil Sci.* **1998**, *163*, 535–543.

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