Sorption and Mobility of ^{14}C-Labeled Imazaquin and Metolachlor in Four Soils As Influenced by Soil Properties

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Aqueous batch-type sorption−desorption studies and soil column leaching studies were conducted to determine the influence of soil properties, soil and suspension pH, and ionic concentration on the retention, release, and mobility of [^{14}C]imazaquin in Cape Fear sandy clay loam, Norfolk loamy sand, Rion sandy loam, and Webster clay loam. Sorption of [^{14}C]metolachlor was also included as a reference standard. L-type sorption isotherms, which were well described by the Freundlich equation, were observed for both compounds on all soils. Metolachlor was sorbed to soils in amounts 2−8 times that of imazaquin, and retention of both herbicides was related to soil organic matter (OM) and humic matter (HM) contents and to herbicide concentration. Metolachlor retention was also related to soil clay content. Imazaquin sorption to one soil (Cape Fear) increased as concentration increased and as suspension pH decreased, with maximum sorption occurring in the vicinity of $pK_{a1} = (1.8)$. At pH levels below pK_{a1} imazaquin sorption decreased as hydronium ions (H_3O^+) increased and competed for sites. NaCl was more effective than water in desorption of imazaquin at pH levels near the pK_{a1}. Mechanisms of bonding are postulated and discussed. The mobility of imazaquin through soil columns was in the order Rion ≥ Norfolk > Cape Fear ≥ Webster, whereas for metolachlor it was Rion ≥ Norfolk ≫ Webster ≥ Cape Fear. Imazaquin was from 2 to 10 times as mobile as metolachlor.

KEYWORDS: Sorption−desorption; soil mobility; imazaquin; metolachlor; soil pH

INTRODUCTION

Imazaquin [2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl]-3-quinolinecarboxylic acid] is an amphoteric herbicide and a member of the imidazolinone chemical family. It controls a wide range of broadleaf weeds when applied postemergence or preemergence or is preplant incorporated (*1*). Imazaquin ionizes, as depicted in **Figure 1**, and has reported pK_a values of 1.8 (NH^+) (*2*), 3.8 (COOH) (*1, 3*), and 10.5 (OH) (*4*). It is moderately water soluble with K_s values ranging from 98 mg/L at pH 4 to 149 mg/L at pH 8 (*4*) and has a low vapor pressure of $<2 \times 10^{-8}$ mmHg at 45 °C (*1*). Low to moderate soil binding K_f values range from 0.2 to 8.8 mL/g (*1*). Liu and Weber (*4*) reported that imazaquin sorption in soils was correlated with organic matter (OM) content and pH, and it was later confirmed by Regitanno et al. (*5*). Sorption of imazaquin and related imidazolinone compounds has also been correlated with soil OM, humic matter (HM), and clay contents (*6−8*), pH (*9, 10*) and OM, and clay contents and pH (*2, 11−13*), as well as hydrous metallic content and pH (*14*), OM and extractable Fe (*6, 15*), and humic acid (HA) and ferrihydrite

(*13, 16, 17*). Sorption increased with increased soil colloid content and with decreased pH.

Imazaquin has been reported to be relatively mobile in soils. Liu and Weber (*4*) reported imazaquin to be more mobile than cinmethylin, a poorly aqueous soluble (K_s = 63 mg/L), nonionizable herbicide, or prometryn, a weakly basic (pK_a = 4.09), poorly aqueous soluble (K_s = 33 mg/L) herbicide, but less mobile than chlorsulfuron, a weakly acidic (pK_a = 3.6), very highly aqueous soluble (31.8 g/L) herbicide in soil leaching columns with OM levels of 1.4−10% and that mobility was inversely related to OM content. Lolas and Galopolous (*18*) reported that imazaquin was more mobile than cinmethylin and metazachlor, a moderately aqueous soluble (450 mg/L), non-ionizable herbicide. Imazaquin was reported by Goetz et al. (*14*) to be more mobile than atrazine, a weakly basic (pK_a = 1.7), poorly aqueous soluble (K_s = 33 mg/L) herbicide, or metribuzin, a very weakly basic (pK_a = 1.0), high aqueous soluble (K_s = 1100 mg/L) herbicide. Basham et al. (*6*) observed that imazaquin mobility in soils was inversely related to OM and clay contents, and Stougaard et al. (*2*) using soil thin layer plates observed that imazaquin mobility was inversely related to pH.

Metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] is a nonionizable substituted acetamide herbicide that controls grasses and some broadleaf weeds and sedges when applied preemergence or preplant

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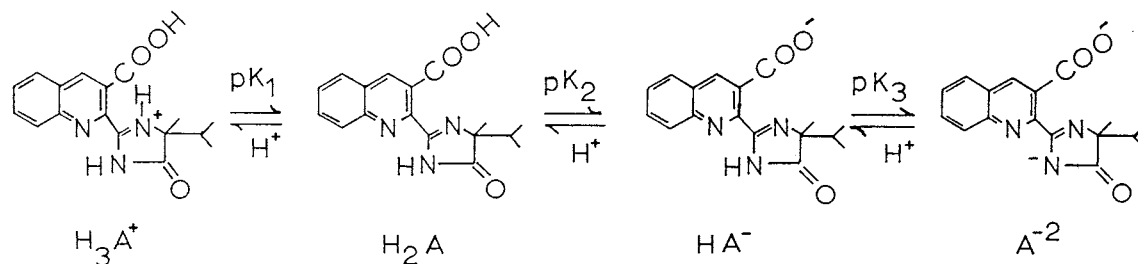† North Carolina State University.
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Figure 1. Ionization of imazaquin.

Table 1. Soil Properties of A_p Horizons from Four Soils

soil series	constituents							reactivity/capacity			
	HM content[a] (g/100 cm³)	OM content[a] (%)	particle size[a]			texture[b]	clay type[c]	pH[d]	CEC[d] (cmol(+)/kg)	bulk density[e] (mg/m³)	pore vol[f] (cm³)
			sand (%)	silt (%)	clay (%)						
Cape Fear	5.4	5.7	52	28	20	scl	MK	4.7	12.7	1.2	316
Norfolk	0.3	1.1	74	18	8	ls	KV	5.9	2.7	1.7	212
Rion	0.1	0.9	60	24	16	sl	K	6.7	3.8	1.6	231
Webster	2.3	4.9	28	45	27	cl	MI	7.4	20.2	1.4	268

[a] North Carolina Department of Agriculture, Soil Testing Laboratory (HM = % humic matter on a volume basis). [b] c = clay, l = loam, s = sand. [c] From X-ray diffraction analysis; K = kaolinite, M = montmorillonite, V = vermiculite, I = illite. [d] A&L Agricultural Laboratories, Omaha, NE (OM = organic matter). [e] Calculated from air-dried soil moderately well packed in the leaching columns. [f] Columns volume = 590 cm³.

incorporated (*1*). It has moderate solubility (K_s = 530 mg/L), moderate to high volatility (VP = 3.1×10^{-5} mmHg at 25 °C), and low soil binding K_d values of 0.1–2.1 mg/L (*1*). Soil retention of metolachlor was reported to be related to OM content (*19–24*), OM and clay contents (*25–30*), and OM and clay contents and surface area (*31*). L-type sorption isotherms resulted when metolachlor and two related acetamides, alachlor and acetochlor, were sorbed by Ca–OM, and S-type isotherms resulted when the chemicals were sorbed by calcium montmorillonite (*21, 25, 32, 33*). L-type or C-type isotherms resulted when the herbicides were sorbed on soils, depending on the OM/clay ratio. Farenhorst et al. (*34*) reported that metolachlor and atrazine were sorbed in similar amounts by earthworm burrow linings and sorption was greater on organic-rich corn and soybean linings than on normal burrow linings. Ding et al. (*35*) reported metolachlor sorption on extracted soil HA and humin increased with aromaticity of the organic fractions and was greater on conservation tillage soils than on conventional tillage soils. Prometryn and diniconazole, a weakly basic (pK_a = 2.6), poorly water soluble (K_s = 40 mg/L) fungicide, were sorbed in greater amounts than the acetamide herbicides by Ca–OM, calcium montmorillonite, and soils (*22, 25, 29*).

The mobility of metolachlor in soils was reported to be inversely related to soil OM and clay contents (*19, 36–39*). However, Novak et al. (*40*) reported that metolachlor leaching to subsurface drains was primarily by preferential flow and was greater in clay soil than in silt soil. In soil leaching columns, metolachlor was more mobile than cinmethylin (*36*); atrazine (*37, 41–43*); terbuthylazine, a weakly basic (pK_a = 1.5), very poorly low water soluble (K_s = 8.5 mg/L) herbicide (*39, 41*); diazinon, a nonionizable, poorly water soluble (K_s = 60 mg/L) insecticide (*44*); and primisulfuron-methyl, a weakly acidic (pK_a = 5.1), poorly water soluble (K_s = 25 mg/L at pH 5.2) herbicide (*42*). Metolachlor was less soil mobile than aldicarb, a nonionizable, highly water soluble (K_s = 6000 mg/L) insecticide (*41*); carbofuran, a nonionizable, moderately water soluble (K_s = 700 mg/L) insecticide (*44*); and dimetheneamid, a nonionizable, highly water soluble (K_s = 1174 mg/L) acetamide herbicide (*45*). It has also been reported to be equal to or greater than

alachlor in soil mobility (*37, 43*). Mobility of the chemicals was generally related to the water solubility of the chemicals.

The objectives of these studies were to (a) compare the relative sorptivities and mobilities of [^{14}C]imazaquin and [^{14}C]-metolachlor on Ap horizon material from Cape Fear sandy clay loam, Norfolk loamy sand, Rion sandy loam, and Webster clay loam, (b) correlate herbicide sorption with selected soil properties, (c) examine the effect of suspension pH on sorption and release of imazaquin from soil, and (d) postulate binding mechanisms of imazaquin by soil colloids.

MATERIALS AND METHODS

Soils. Soil samples were collected from the Ap horizon (0–15 cm) from four locations: a Cape Fear sandy clay loam (*Typic Umbraquult*; fine-loamy, siliceous, thermic) from the Tidewater Research Station, Plymouth, NC; a Norfolk loamy sand (*Typic Paleudult*; fine-loamy, siliceous, thermic) from the Upper Coastal Plains Research Station, Rocky Mount, NC; a Rion sandy loam (*Typic Hapludult*; fine-loamy, mixed thermic) from the Upper Piedmont Research Station, Reidsville, NC; and a Webster clay loam (*Typic Haplaquoll*; fine-loamy, mixed, mesic) from near Webster City, IA. The soils were air-dried, passed through a 4-mm mesh screen, and stored in sealed containers.

Soil properties including %OM (chromic acid oxidation method) (*46*), pH (1:1 soil/water), soil particle size (hydrometer method) (*47*), and cation exchange capacity (CEC) (1.0 M ammonium acetate replacement method) (*48*) were determined by A&L Agricultural Laboratories, Omaha, NE. Soil humic matter (HM) was determined by the North Carolina Department of Agriculture, Raleigh, NC, using a NaOH/DTPA/C_2H_5OH extraction method (*49*). Clay types were determined using X-ray diffraction techniques (*50*). Properties of the soils used in sorption and leaching studies are summarized in **Table 1**. Soil pH ranged from strongly acid (4.7) for the Cape Fear soil to slightly alkaline (7.4) for the calcareous Webster soil; both soils contained high OM and HM contents and moderate contents of expanding type clays. Norfolk and Rion soils were moderately acidic and low in OM, HM, and clay contents, with nonexpanding type clays. The former soils were lighter (lower bulk density) and had higher nutrient holding capacity (CEC) and water holding capacity (pore volume) than the latter soils. Among soil properties, OM content was correlated to HM content (r = 0.92*), both were correlated with pore volume (r = 0.93* and 0.99***, respectively), and both were inversely correlated with bulk

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density ($r = -0.95**$ and $-0.96**$, respectively). Clay content was correlated with CEC ($r = 0.93*$), and bulk density was inversely correlated with pore volume ($r = -0.99***$).

Sorption. Aqueous imazaquin and metolachlor stock solutions of 40 μM (2000 dpm/mL) were prepared using technical grade (98%) and ^{14}C-ring-labeled materials with specific activities of 0.544 and 0.969 TBq/kg, respectively. From the stock solutions of each herbicide, concentrations of 5, 10, 20, and 40 μM were prepared. For study 1, a 20.0-mL aliquot of each concentration for each herbicide was added to nonsorptive polypropylene centrifuge tubes. Ten grams of each soil was added to the respective tubes, and the tubes were sealed and placed on a horizontal shaker with 140 oscillations/min for 24 h at 25 °C. Controls (soil in deionized water) and standards were included for calibration and background correction purposes. Samples were removed from the shaker and centrifuged for 10 min at 12000 rpm, after which a 1.0-mL aliquot of the supernatant was removed from under the liquid surface of each tube and added to 15.0 mL of scintillation cocktail (Scintiverse E, Fisher Scientific Co., Springfield, NJ), and radioactivity was assayed by liquid scintillation spectrometry (LSS) (Packard TRI-CARB liquid scintillation analyzer, model 2000CA, Packard Instrument Co., Downers Grove, IL). Samples were counted for 10000 counts or 10 min, and counting efficiencies ranged from 89 to 96% after correction to dpm. Amount of herbicide sorbed by soil was determined by difference between initial (C_i) and equilibrium (C_e) concentrations. A completely randomized design with three replications, which was repeated, was employed. Statistical analyses (ANOVA followed by LSDs and correlation analysis) were performed using SAS procedures (*51*). Asterisks denote the level of significance, that is, 10% (*), 5% (**), and 1% (***). Retention of herbicides by soils was determined by calculating herbicide distribution coefficients (K_d), where $K_d = x/m$ (nmol/g herbicide sorbed to soil) $\div$ C_e (nmol/mL herbicide in equilibrium solution). The Freundlich equation ($x/m = K_f C_e^{1/n}$), where K_f = capacity constant and $1/n$ = intensity constant (slope), was also used to describe sorption isotherms.

Effects of pH on Sorption/Desorption. The effects of suspension pH on imazaquin sorption were also determined for the Cape Fear soil. In study 2, the pH values of the 20-mL tubes of 40 μM stock solution were adjusted with concentrated HCl to provide suspension pH levels of 5.1, 3.1, 1.9, and 1.5. Sorption was carried out as described previously. Study 3 was conducted using 0.2 g of soil, 20 mL of 0.059 μM solution at 25 °C, and pH levels of 7.1, 4.2, 2.3, and 1.5 with an exposure time of 4 h to reach equilibrium. Equilibrium was reached more rapidly as the pH was lowered and occurred within a matter of minutes at pH 1.5 (data not shown). Duplicate soil pellets were desorbed with 20 mL of deionized water or 0.1 M NaCl for 8 h to reach equilibrium. Desorption was also more rapid at low pH. Corrections were made for the solution remaining in pellets during the sorption phase, and the amount of herbicide desorbed was then calculated. Study 4 was performed using 0.2 g of soil, 20 mL of each of two concentrations (0.032 and 0.063 μM) at 25 °C, and pH levels of 4.9, 4.5, 3.7, 3.0, 2.5, 2.0, 1.4, and 1.1 at exposure times of 1 h. One milliliter of solution was removed and radioassayed at each pH level. Each study utilized a completely randomized design with three replications, which was repeated. Statistical analyses (ANOVA followed by LSDs and correlation analysis) were performed using SAS procedures (*51*). Asterisks denote the level of significance as previously mentioned.

Mobility. Air-dried soils (708, 1003, 944, and 826 g, respectively, of Cape Fear, Norfolk, Rion, and Webster) were packed in cellulose acetate butyrate columns, which were determined to be nonsorptive for the herbicides. Columns 35 cm long with a 5-cm diameter (590 cm³ volume) were constructed following the procedures of Weber et al. (*52*). Soil columns were subirrigated until the soil surface was wet and then allowed to drain freely for 24 h. Technical grade imazaquin was mixed with 0.109 MBq of ^{14}C-ring-labeled imazaquin, and technical grade metolachlor was mixed with 0.117 MBq of ^{14}C-ring-labeled metolachlor to yield 0.14 and 2.24 kg of ai/ha rates of application, respectively. The herbicides were applied by pipet in 8.0 mL of deionized water in a crosshatched fashion to the soil surfaces of the soil columns. Nylon mesh was placed on the top of the soil surfaces to maintain level surfaces, and columns were covered with aluminum foil

to prevent evaporation. Erlenmeyer flasks were placed beneath soil columns to catch leachate, which was collected twice daily. Twenty-five milliliters of water was applied to each of the columns four times daily in 4-h intervals at 8:00 a.m. and 12:00, 4:00, and 8:00 p.m. Leachate collection flasks were weighed, and a 1.0-mL sample was taken from each flask and added to 15.0 mL of scintillation cockail and assayed by LSS, as previously described.

After 10 days, a total of 1 L (50 cm depth equivalent) of water had been added to the columns. Columns were then split longitudinally and divided into six 5-cm sections (0−5, 5−10, 10−15, 15−20, 20−25, and 25−30 cm). Each section was bagged and thoroughly mixed and a 2-g subsample drawn for moisture determination. Two 1.0-g subsamples were combusted using a biological oxidizer (OX-300 automated biological oxidizer, R. J. Harvey Instrument Co., Hillsdale, NJ), and the ^{14}CO$_2$ was trapped in 15 mL of Harvey ^{14}C scintillation cocktail, which was assayed by LSS. Total ^{14}C recovery in soil and leachate ranged from 75 to 105%, and samples varying by >20% were rerun. Amounts of herbicide recovered from each column were normalized to 100% of total applied. A mobility index (MI) was calculated for each herbicide−soil column for ease of comparison by summing the mean depth (D) (2.5, 7.5, 12.5, 17.5, 22.5, and 27.5 cm) of each section, that is, the distance the chemical moved, multiplied by the normalized fraction (F) of chemical present in each section; that is, MI = $\sum D \times F$. Herbicide present in leachate was added to the fraction found in the bottom 27.5-cm section. The maximum value (MI$_{max}$) is obtained if all of the chemical (F = 1.00) is distributed in the bottom (27.5 cm) section or in the leachate; that is, MI$_{max}$ = (27.5) × (1.0) = 27.5. The smallest (MI$_{min}$) value is obtained if all (F = 1.00) of the chemical is retained in the uppermost (2.5 cm) section; that is, MI$_{min}$ = (2.5)(1.0) = 2.5.

The experimental design was a completely randomized design with two replications, and the experiment was repeated. Leachate data were subjected to analysis of variance, and means were compared using the LSD at the 5% level following SAS procedures (*51*). Asterisks denote the level of significance.

All ^{14}C wastes were disposed of by the North Carolina State University Life Safety Services following proper procedures (*53*).

RESULTS AND DISCUSSION

Sorption. Imazaquin and metolachlor sorption isotherms were of the L-type (*54*) for both herbicides on all four soils, with the latter being sorbed in 2−8 times the amounts as the former, as indicated by K_d and K_f values and K_d metolachlor/K_d imazaquin and K_f metolachlor/K_f imazaquin ratios for study 1. The results are given in **Table 2**. The sorption isotherms were well described by the Freundlich equation. Our K_d values for the two herbicides fell within the range reported in the literature (*1, 3*), that is, imazaquin (lit. = 0.2−6.5; ours = 0.16−1.7), metolachlor (lit. =0.1−10.0; ours = 0.57−5.7). Our K_f values also fell within the range reported in the literature, (*1, 3*), that is, imazaquin (lit. = 0.2−8.8; ours = 0.6−2.4), metolachlor (lit. = 0.1−26.7; ours = 1.3−5.6).

For imazaquin, the order of sorption by the soils was Cape Fear ≫ Webster ≫ Norfolk > Rion, as defined by K_d and K_f values, which were correlated with soil OM ($r = 0.97***$ and $0.97***$, respectively), HM ($r = 0.97***$ and $0.97***$, respectively), and CEC ($r = 0.73**$ and $0.73**$, respectively).

For metalochlor, the order of sorption was Webster > Cape Fear ≫ Norfolk ≫ Rion, as defined by K_d and K_f values, which were highly correlated with OM ($r = 0.95***$ and $0.96***$, respectively), HM ($r = 0.75**$ and $0.78**$, respectively), clay contents ($r = 0.83***$ and $0.79**$, respectively), and CEC ($0.96***$, and $0.94***$, respectively). Soil OM and HM were also correlated with each other ($r = 0.92*$), as was percent clay and CEC ($r = 0.93*$). These findings are in agreement with those reported in the literature, as previously discussed.

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Table 2. Herbicide/Soil Distribution (K_d) Values, Freundlich K_f and $1/n$ Values, and K_d and K_f Ratios for Aqueous Sorption of ^{14}C-Labeled Imazaquin and Metolachlor by Four Soils (Study 1) (C_i = 5, 10, 20, 40 μM; 20 mL; 10 g; 25 °C; 24 h)

soil	imazaquin (I) equil concn (C_e) (nmol/mL)	K_d (mL/g)	K_f (mL/g)	$1/n$	metolachlor (M) equil concn (C_e) (nmol/mL)	K_d (mL/g)	K_f (mL/g)	$1/n$	K_d(M)/K_d(I) ratio	K_f(M)/K_f(I) ratio
Cape Fear	2.7	1.70			1.5	4.67			2.7	
	5.9	1.39			3.3	4.06			2.9	
	12.6	1.17			6.5	4.15			3.5	
	27.0	0.96			13.8	3.80			3.9	
mean		1.34				4.17			3.1	
extrp 1.0[a]			2.4	0.72			5.0	0.87		2.1
Norfolk	4.0	0.50			2.8	1.57			3.1	
	8.4	0.38			5.7	1.51			4.0	
	17.0	0.35			12.4	1.23			3.5	
	36.2	0.21			26.1	1.07			5.1	
mean		0.36				1.35			3.8	
extrp 1.0[a]			0.8	0.63			2.2	0.79		2.7
Rion	4.2	0.38			3.3	1.03			2.7	
	8.7	0.30			7.1	0.82			2.7	
	18.0	0.22			14.9	0.68			3.1	
	37.0	0.16			31.1	0.57			3.6	
mean		0.26				0.78			3.0	
extrp 1.0[a]			0.6	0.40			1.3	0.76		2.2
Webster	3.3	1.03			1.3	5.69			5.5	
	6.8	0.94			2.8	5.14			5.5	
	14.2	0.82			5.8	4.90			6.0	
	30.4	0.63			11.8	4.78			7.6	
mean		0.86				5.13			6.0	
extrp 1.0[a]			1.7	0.71			5.6	0.94		3.3
mean for all soils		0.70	1.4	0.61		2.86	3.5	0.84	4.1	2.6
LSD 0.05		0.09				0.26				

[a] Extrapolated to equilibrium concentration 1.0 nmol/mL from Freundlich equation.
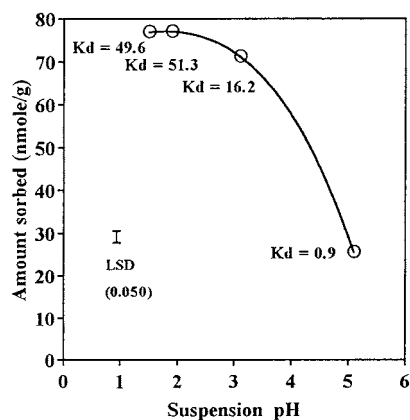
Figure 2. Suspension pH effect on imazaquin sorption on Cape Fear soil (study 2) (C_i = 40 nmol/mL, 20 mL, 10 g, 25 °C, 24 h).
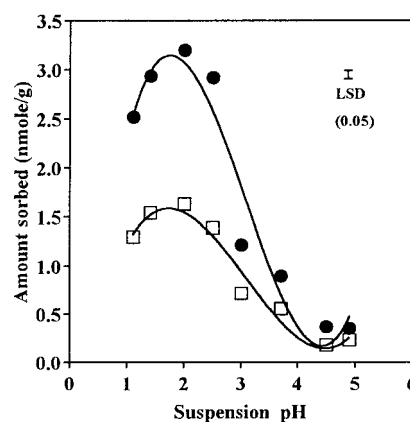
Figure 3. Suspension and pH and imazquin concentration effect on sorption of imazaquin on Cape Fear soil (study 4) (top, C_i = 0.063 nmol/mL; bottom, C_i = 0.032 nmol/mL, 20 mL, 0.2 g, 25 °C, 1 h).

Suspension pH Effects on Sorption/Desorption of Imazaquin. Sorption of imazaquin by Cape Fear soil increased greatly as suspension pH decreased in each of the three pH studies (**Figures 2** and **3** and **Table 3**). Using the same experimental conditions as were used in study 1, and using only 40 μM concentrations, which were reduced in pH, study 2 illustrated the great effect that reduced pH had on imazaquin sorption to the Cape Fear soil (**Figure 2**). K_d values increased by 20−60,

times and a maximum appeared to occur in the vicinity of pK_{a1} = 1.8 of the herbicide.

Utilizing slightly different laboratory conditions and greatly reduced imazaquin concentrations of 0.059 nmol/mL and soil quantities of 0.2 g, study 3 revealed that lowering the suspension pH increased imazaquin sorption by the soil by 30−50 times and that 0.1 NaCl was 30−60 times more effective than water in desorbing the compound (**Table 3**). These two phenomena

Table 3. Suspension pH Effect on Sorption/Desorption of Imazaquin by Cape Fear Sandy Loam (Study 3) (C_i = 0.059 μM; 20 mL; 0.2 g; 25 °C; 4 h Sorption; 8 h Desorption)

suspension pH	amount sorbed (nmol/g)	K_d (mL/g)	amount desorbed[a]				species present initially[b]		
			with water (nmol/g)	with 0.1 M NaCl (nmol/g)	difference[c] (nmol/g)	%	H_3A^+ (%)	H_2A (%)	HA^- (%)
7.1	0.21	3.7	0.16				0	0	100
	0.20	3.5		0.18	0.02	13	0	0	100
4.2	0.23	4.0	0.17				0	4	96
	0.22	3.9		0.18	0.01	6	0	4	96
2.3	3.86	189.2	1.12				20	61	19
	3.85	187.8		1.44	0.32	29	20	61	19
1.5	3.08	109.2	0.61				65	33	2
	3.08	109.2		0.96	0.35	57	65	33	2
LSD 0.05	0.18	3.1	0.09	0.09	0.09				

[a] Total for two desorptions each. [b] pK_a values of 1.8, 2.8, and 10.5 (0% A^{-2} at all pH levels). Percentages present calculated from expressions: $K_{a1}/H^+ = H_2A/H_3A^+$, $K_{a2}/H^+ = HA^-/H_2A$, $K_{a3}/H^+ = A^{-2}/HA^-$, and $H_3A^+ + H_2A + HA^- = 1$. [c] Increase in imazaquin released using 0.1 M NaCl over that of water.

suggest that as pH was reduced imazaquin protonated to the H_3A^+ form shown in **Figure 1** in quantities presented in **Table 3** and sorbed to the soil colloids through cation exchange reactions, as confirmed by the much greater effectiveness of 0.1 M Na^+ over that of water in displacing imazaquin.
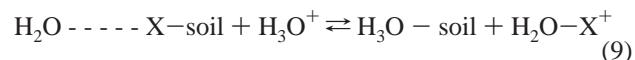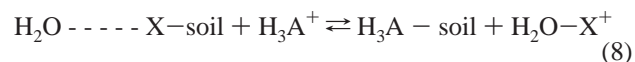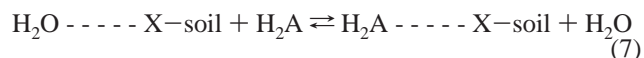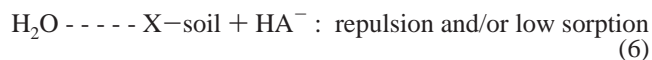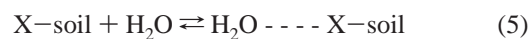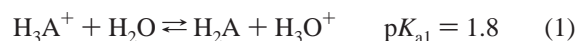
To further elucidate the mechanism of bonding of imazaquin under low pH conditions, study 4 was carried out using two imazaquin concentrations and the pH was lowered to 1.1. **Figure 3** depicts the results; that is, sorption of imazaquin by the soil was dependent on imazaquin and hydronium (H_3O^+) concentration and reached a maximum at a pH in the vicinity of the pK_{a1} of the compound.

Greater sorption of imazaquin by soil clays with reduced suspension pH in the range of pH 2−4 was reported previously (*4*, *11*, *12*) and attributed primarily to H-bonding of the imazaquin molecule and to some ionic binding of imazaquin cations. Sorption of imazaquin in suspensions below pH 2 accompanied by much greater desorption with salt solution than with water is indicative of ionic bonding and cation exchange. The phenomenon, along with maximal sorption in the vicinity of the pK_a, has been reported for numerous weakly basic herbicides (*55*), weakly basic enzymes and proteins (*56*, *57*) and purine, pyrimidines, and nucleosides (*58*, *59*). Reduction of weakly basic cations at pH levels below their pK_a values has been attributed to competition from high H^+ ion concentrations (H_3O^+ ions) (*55*, *59*) and/or Al^{3+} ions (*60*).

Mechanisms of Bonding. Correlation analysis of imazaquin sorption by Cape Fear soil versus the species present in suspension at each pH (**Table 1** for soils in study 1; **Figure 2** for study 2; **Table 3** for study 3) indicates that sorption was most highly correlated with percent cationic (H_3A^+) species present at each pH plus molecular species that become cationic upon contact with H^+ on the colloidal surfaces [$r = 0.85$*, study 1 (**Table 2**); $r = 0.99$**, study 2 (**Figure 2**); $r = 0.99$**, study 3 (**Table 3**)]. Sorption was also correlated with percent cationic species (percent H_3A+) only in study 2 ($r = 0.99$**) and study 3 ($r = 0.99$**). Sorption was inversely correlated with percent anionic (HA^{-1}) species present at each pH [$r = -0.85$*, study 1 (**Table 2**); $r = -0.95$**, study 2 (**Figure 2**); $r = -0.99$**, study 3 (**Table 3**)], probably because negatively charged species were repelled from negatively charged surfaces. However, small amounts of imazaquin anions have been reported to be sorbed to positively charged surfaces in soils (*14*) and synthetic ferrihydrites (*13*, *16*).

Ionization of imazaquin, as shown in **Figure 1**, is depicted in eqs 1−3, ionization of water in eq 4, and hydration of soil in

eq 5. Postulated mechanisms of bonding of the herbicide by soil colloids are depicted in eqs 6−11.

$$H_3A^+ + H_2O \rightleftarrows H_2A + H_3O^+ \qquad pK_{a1} = 1.8 \qquad (1)$$

$$H_2A + H_2O \rightleftarrows HA^- + H_3O^+ \qquad pK_{a2} = 3.8 \qquad (2)$$

$$HA^- + H_2O \rightleftarrows A^{-2} + H_3O^+ \qquad pK_{a3} = 10.5 \qquad (3)$$

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^- \qquad pK_w = pK_a + pK_b = 14 \qquad (4)$$

$$X-soil + H_2O \rightleftarrows H_2O----X-soil \qquad (5)$$

$$H_2O-----X-soil + HA^- : \text{repulsion and/or low sorption} \qquad (6)$$

$$H_2O-----X-soil + H_2A \rightleftarrows H_2A-----X-soil + H_2O \qquad (7)$$

$$H_2O-----X-soil + H_3A^+ \rightleftarrows H_3A - soil + H_2O-X^+ \qquad (8)$$

$$H_2O-----X-soil + H_3O^+ \rightleftarrows H_3O - soil + H_2O-X^+ \qquad (9)$$

$$H_3O - soil + H_3A^+ \rightleftarrows H_3A - soil + H_3O^+ \qquad (10)$$

$$H_3O-soil + H_2A \rightleftarrows H_3A - soil + H_2O \qquad (11)$$

In eqs 1−11 H_3A^+ = imazaquin cation, H_2A= imazaquin molecule, H_3O^+ = hydronium (hydrated hydrogen) ion, H_2O = water molecule, HA^- = monovalent imazaquin anion, A^{-2} = divalent imazaquin anion, OH^- = hydroxide ion, X−soil = X−inorganic cations bound to the exchange complex of dry soil colloids, H_2O - - - - - X−soil = hydrated X−inorganic cations bound to soil colloids, H_2A- - - - - soil = molecular imazaquin physically sorbed to soil, H_3A−soil = cationic imazaquin ionically bound to soil, H_2O-X^+ = hydrated displaced inorganic cations, and H_3O−soil = hydronium ion ionically bound to soil colloids.

Equation 6 represents repulsion of imazaquin by negatively charged soil colloids and/or low sorption to positive charges on colloids with measurable anion exchange capacity. Equation 7 represents imazaquin molecules physically bound to clay colloids under slightly acid conditions where the pH at the colloidal surface is 2−3 times lower than that in the bulk
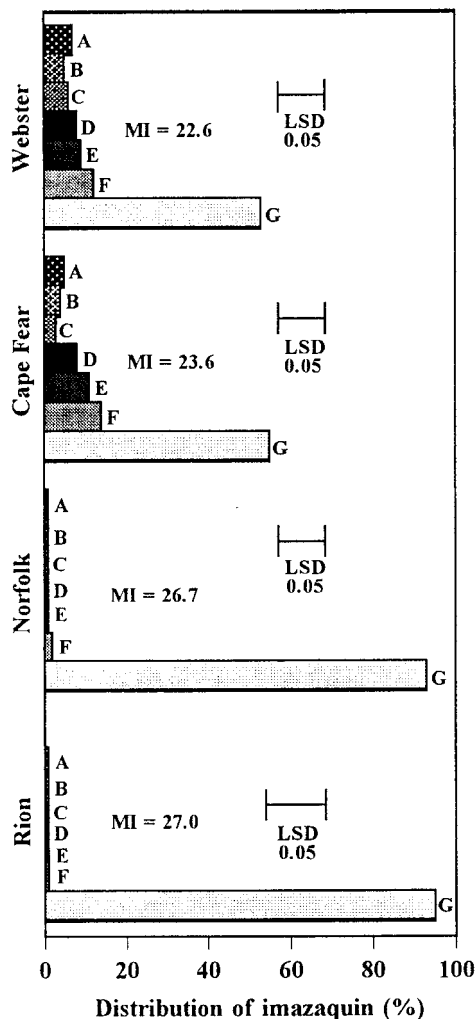
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Figure 4. Distribution of ^{14}C in [^{14}C]imazaquin-treated soils after leaching with 50 cm of water (100 mL/day for 10 days, saturated/unsaturated flow, pore volumes of water applied = 4.3, Rion; 4.7, Norfolk; 3.2, Cape Fear; 3.7, Webster) (A = 0–5 cm, B = 5–10 cm, C = 10–15 cm, D = 15–20 cm, E = 20–25 cm, F = 25–30 cm, G = leachate).

Figure 5. Distribution of ^{14}C in [^{14}C]metolachlor-treated soils after leaching with 50 cm of water (100 mL/day for 10 days, saturated/unsaturated flow, pore volumes of water applied = 4.3, Rion; 4.7, Norfolk; 3.2, Cape Fear; 3.7, Webster) (A = 0–5 cm, B = 5–10 cm, C = 10–15 cm, D = 15–20 cm, E = 20–25 cm, F = 25–30 cm, G = leachate).

suspension, as described by Harter and Alrichs (*61*), or bound to organic colloids through H-bonds, charge-transfer complexes, or hydrophobic bonds as suggested by Senesi (*62*). Equation 8 represents cation exchange of imazaquin cations by the soil exchange complex in exchange for hydrated inorganic cations at suspension pH levels <3.8. Equation 9 represents cation exchange between hydronium ions and hydrated inorganic cations on the soil exchange complex at low pH. Equation 10 represents competitive cation exchange between imazaquin cations and hydronium ions by the soil exchange complex at pH levels in the vicinity of pK_{a1}, as regulated by imazaquin and hydronium concentrations. Equation 11 represents direct protonation and coulombic binding of imazaquin molecules at acidic sites on soil colloids. Equations 8 and 9, when driven to the left in desorption studies utilizing 0.1 M NaCl, represent the replacement of imazaquin cations and/or hydronium ions on the soil exchange complex by the high concentration of Na^+ cations.

Retention of metolachlor by the soils was probably by way of hydrophobic bonding to lipophilic sites on OM and HM, as suggested by Kozak et al. (*22*) and Nègre et al. (*8*), and to hydrophilic clay colloids through H-bonds, charge-transfer
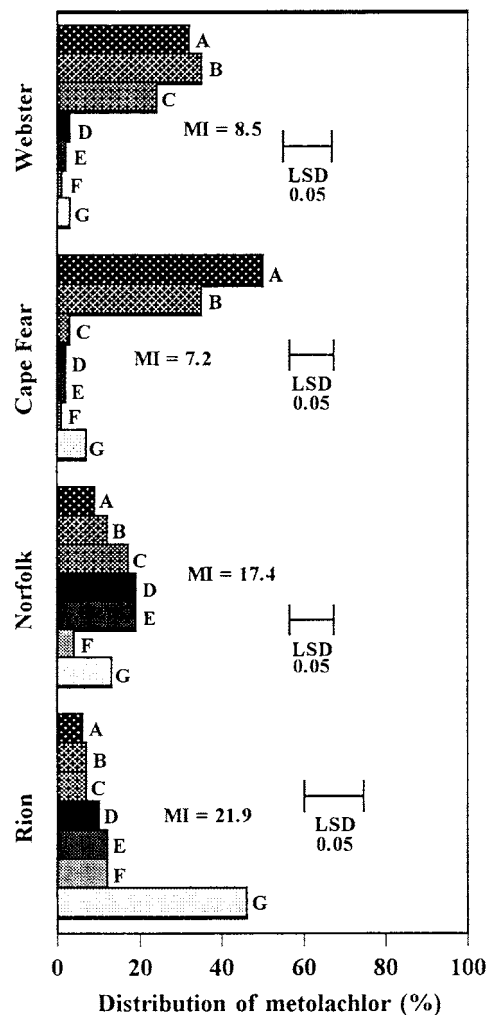
mechanisms, or van der Waals forces, as suggested by several investigators (*31, 60, 62*).

Mobility. Total ^{14}C detected in leachate from [^{14}C]imazaquin- and [^{14}C]metolachlor-treated soil leaching columns of the four soils is shown in **Figures 4** and **5**, respectively. Imazaquin was found in leachate from Rion, Norfolk, Cape Fear, and Webster soils in 2, 7, 8, and 18 times greater amounts, respectively, than metolachlor. More than 90% of [^{14}C]imazaquin leached through the Rion and Norfolk soils, as compared with 13 and 46%, respectively, for [^{14}C]metolachlor. Approximately 50% of [^{14}C]-imazaquin leached through the Cape Fear and Webster soils, as compared to <7% for [^{14}C]metolachlor.

The order of mobility of the two herbicides through the four soils was as follows: For imazaquin, Rion = Norfolk ≫ Cape Fear = Webster, as determined by MI values of 27.0, 26.7, 23.6, and 22.6, respectively, which were inversely correlated with soil OM ($r = -0.95***$), HM ($r = -0.74**$), and clay ($r = -0.87***$) contents, as also reported in the literature (*4, 6*), and CEC ($r = -0.98***$) and pore volume ($r = -0.78**$) (**Figure 4** and **Table 1**). Imazaquin mobility was also correlated with soil bulk density ($r = 0.81**$). For metolachlor, Rion > Norfolk ≫ Webster = Cape Fear, as determined by MI values of 21.9, 17.4, 8.5, and 7.2, respectively, which were inversely related to soil OM ($r = -0.97***$), HM ($r = -0.87***$), and clay

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($r = -0.67*$) contents, as also reported in the literature (*19, 36–39*), and CEC ($r = -0.85***$) and pore volume ($r = -0.84***$) (**Figure 5** and **Table 1**). Metolochlor mobility was also correlated with soil bulk density ($r = 0.86***$).

CEC was correlated with percent clay content of the soils ($r = 0.93*$), and OM and HM contents were correlated with soil pore volume ($r = 0.93*$ and $0.99***$, respectively) (**Table 1**). Bulk density was inversely related to OM ($r = -0.95**$) and HM ($r = -0.96***$) contents and with pore volume ($r = -0.99***$).

Imazaquin MI values for the four soils were highly inversely related to soil K_d and K_f values ($r = -0.86***$ and $-0.86***$, respectively), as was also the case for metolachlor ($r = -0.96***$ and $-0.98***$, respectively).

SUMMARY AND CONCLUSIONS

Imazaquin sorption in four soils increased as HM, OM, and clay contents increased and pH decreased. Molecular species were sorbed to HM, OM, and clay surfaces through physical bonding mechanisms (*2, 4–7*), whereas anionic species were repelled by these constituents but were probably sorbed to positively charged sites of metallic hydrous oxides through ionic bonds (*6, 13–15, 17*). Cation species of imazaquin formed at very low pH or at acidic surfaces were bound through cation exchange forces (*4, 11*). Reported complexes of imazaquin to mixtures of soil constituents may also have occurred (*4, 8, 11–13, 16*). The mobility of imazaquin increased as HM, OM, and clay contents of the soils decreased (*4, 6*) and as pH increased (*2*), due to the inverse relationship between mobility and soil retention of the compound. Imazaquin was much more mobile than metolachlor and is reported to be more mobile in soils than weakly basic herbicides such as atrazine (*14*), metribuzin (*14*), and prometryn (*4*) or nonionizable herbicides such as cinmethylin (*4, 18*) and metazachlor (*18*) but more mobile than weakly acidic, high aqueous soluble herbicides such as chlorsulfuron (*4*).

Metolachlor sorption in four soils increased as HM, OM, and clay contents increased, and binding was principally through physical forces between metolachlor molecules and soil constituent surfaces (*25, 31*). Bonding was probably greater between metolachlor and lipophilic surfaces of HM and OM than between the herbicide and polar surfaces of clay minerals. Sorption of nonionizable metolachlor in the four soils was much greater than weakly acidic imazaquin. Sorption was reported to be lower than weakly basic herbicides such as prometryn and diniconazole and related acetanilide compounds and was inversely related to the aqueous solubilities of the latter (*22, 25, 29*). The mobility of metolachlor increased as HM, OM, and clay contents of the four soils decreased and was inversely related to its retention by the soil constituents. It was less mobile than imazaquin and was reportedly more mobile than weakly basic herbicides such as atrazine and terbuthylazine and nonionizable, poorly to very poorly aqueous soluble, pesticides such as chlorothalonil, cinmethylin, and diazinon (*4*). Imazquin and metolachlor are likely to be relatively mobile in sandy soils with OM contents of <2% (*59*) and are ranked as poorly and moderately mobile, respectively, in soils in general (*63*). Lower mobility ranking of imazaquin is due to its shorter half-life.

ACKNOWLEDGMENT

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