

Influence of Soil pH–Sorption Interactions on Imazethapyr Carry-over

Gail A. Bresnahan

Department of Plant Sciences, Loftsgard Hall, North Dakota State University, Fargo, North Dakota 58105

William C. Koskinen

Soil and Water Management Research Unit, Agricultural Research Service, U.S. Department of Agriculture, Room 439, 1991 Upper Buford Circle, St. Paul, Minnesota 55108

Alan G. Dexter

Department of Plant Sciences, Loftsgard Hall, North Dakota State University, Fargo, North Dakota 58105

William E. Lueschen

Department of Agronomy and Plant Genetics, 411 Borlaug Hall, University of Minnesota, St. Paul, Minnesota 55108

Soil pH affects imazethapyr sorption–desorption, which in turn can affect persistence and bioavailability. Long-term imazethapyr carry-over has been observed in soil that is below pH 6.5, resulting in significant sugarbeet damage. Imazethapyr concentration decreased rapidly in field soil, regardless of pH. Despite similar amounts of imazethapyr remaining in aged soils at different pH levels, there were differences in bioavailability, which can be explained by sorption–desorption. At low pH more imazethapyr was sorbed than at high pH, but it readily desorbed. At high pH less imazethapyr was sorbed initially, but it did not readily desorb. Thus, after 3 months, the remaining imazethapyr in low-pH soil was desorbable and bioavailable, resulting in injury to canola and sugarbeet. Liming aged, low-pH soil released bound imazethapyr residues, which would then be degraded and result in less carry-over.

Keywords: *Imazethapyr; sorption; desorption; aged residues*

INTRODUCTION

One of the most important processes affecting the fate of herbicides in the field is sorption. Sorption controls the availability of the herbicide to the target plant and soil microorganisms and the movement of the chemical through the soil profile. Sorption is affected by a number of soil properties and by the nature of the chemical. Soil organic carbon (OC) content is the most important soil property for nonpolar, nonionizable organic chemicals (Koskinen and Harper, 1990). For polar, ionizable chemicals, such as weak acids such as imazethapyr, the most important factor affecting sorption is pH, but at lower pH levels sorption can also be influenced by soil OC content (Oliveira et al., 1999).

Sorption of pesticides has been shown to be affected by aging in soil (Boesten and Van der Pas, 1983; McCall and Agin, 1985; Pignatello et al., 1993; Cox et al., 1998). For instance, sorption of imidacloprid significantly increased during a 16-week incubation period (Cox et al., 1998). The increase in sorption with time would result in decreased availability for movement and microbial degradation.

Imazethapyr is an amphoteric compound due to the presence of both acidic and basic functional groups (Figure 1). The ionizable carboxyl group for imazethapyr has a pK_a value of 3.9 (Renner et al., 1988; Stougaard et al., 1990). At soil pH greater than the pK_a , imazethapyr should exist predominantly in an anionic form ($-\text{COO}^-$), which will be repulsed by the negative charges of the soil colloid, resulting in low sorption on neutral or higher pH soils (Che et al., 1992; Green, 1974). At lower pH conditions, the imazethapyr nitrogen group may be protonated ($pK_a = 2.1$), resulting in a positively charged molecule (Wepplo, 1991). This positive charge is then susceptible to cationic binding with the soil colloid (Stougaard et al., 1990). Also at lower pH levels the presence of uncharged nonionic molecules ($-\text{COOH}$) increases, allowing for increased interaction with the negative charges on the soil colloid (Che et al., 1992; Renner et al., 1988).

A study by Loux and Reese (1993) suggested that, depending on soil type, imazethapyr persistence increases as soil pH decreases. Soils that contain a high OC content and a higher clay content were found to increase imazethapyr persistence (Goetz et al., 1990; Loux et al., 1989). Long-term persistence of imazethapyr may result in injury to nontarget plants by carrying over

* Corresponding author [telephone (701) 231-8894; fax (701) 231-8474; e-mail bresnaha@badlands.nodak.edu].

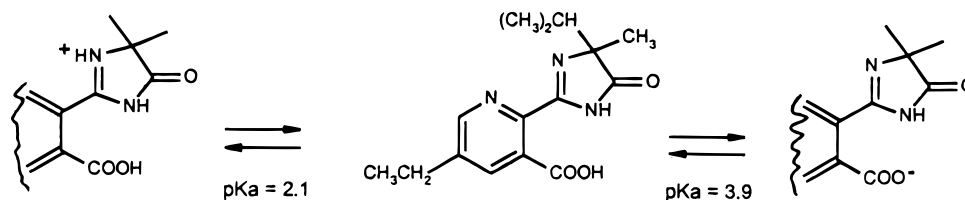


Figure 1. Imazethapyr protonation/ionization.

in years following herbicide application. Imazethapyr carry-over limits the choices of rotational crops. For instance, sugarbeet (*Beta vulgaris* L.) is the crop most susceptible to imazethapyr, and $0.54 \mu\text{g kg}^{-1}$ imazethapyr in soil will cause injury. Turnip (*Brassica rapa* L.) is injured by $1.03 \mu\text{g kg}^{-1}$ imazethapyr and rapeseed (*Brassica napus* L.) by $3.30 \mu\text{g kg}^{-1}$. Grain sorghum (*Sorghum bicolor* L.) is less sensitive at $5.68 \mu\text{g kg}^{-1}$, but it has been injured by imazethapyr carry-over (Onofri, 1996).

The objective of this research was to determine the influence of soil pH/sorption interactions as a function of aging on imazethapyr soil carry-over as indicated by sugarbeet injury. A secondary objective was to determine if increasing the soil pH with spent lime would decrease sorption of aged imazethapyr residues and subsequent potential carry-over.

MATERIALS AND METHODS

Field Experiment—1996. Two field locations in southern Minnesota were used in the experiment. Field 1 soil was Ves soil (fine-loamy, mixed, mesic Calcic Hapludolls). Field 2 soil was a combination of Ves soil and Webster (fine-loamy, mixed superactive, mesic Typic Endoaquolls). Soil texture was determined according to a hydrometer method (Gee and Bauder, 1986). Soil pH levels, measured in a 1:1 w/w soil/deionized water mixture, were 5.1–6.0. The soil OC content, determined using a loss-on-ignition method (Ball, 1964), ranged from 2.1 to 2.3%.

The fields were divided into 7.6×16.8 m plots. Plots were limed at 8 and 26 t ha^{-1} with spent calcium carbonate (equivalent to 7 and 22 t ha^{-1} of virgin lime) from a nearby sugarbeet processing plant or left unlimed. A randomized complete block design with four replicates was used. Field 1 was seeded in 56-cm rows with Pioneer 9137 soybean. Field 2 was seeded in 56-cm rows with Land O Lake 0946 soybean. Imazethapyr was applied at 0.07 kg ha^{-1} to the middle 15.2×6.1 m of each plot when the soybeans were at the 3–4-trifoliolate leaf stage. Samples from the surface 15 cm of soil were collected from limed and unlimed plots at three times during the growing season: immediately after application of the herbicide and at 9 and 18 weeks after application. Five samples were taken from each plot and combined, large particles of foreign matter were removed, and soil was screened using a 20 mesh Micrometer 850 sieve. Soil samples were frozen at $-10 \text{ }^\circ\text{C}$ until analyzed for pH and imazethapyr residues.

Field Experiment—1997. Field 1 was seeded with Viking sugarbeet in 56-cm rows. Sugarbeet was hand-harvested from one row 3 m in length. After washing and weighing, roots were analyzed for sugar and quality parameters, that is, sodium, potassium, and amino N contents, using a modification of the analyses outlined by Carruthers and Oldfield (1961) at the American Crystal Sugar Co.'s laboratory, East Grand Forks, MN. Field 2 was solid-seeded to Pioneer 2375 wheat.

Field Experiment—1998. Field 2 was seeded with American Crystal 309 sugarbeet in 56-cm rows. Yield data were obtained by hand-harvesting two rows 3 m in length. The sugarbeet root yield was determined, and sugarbeet was analyzed for percent sucrose as previously described.

Soil Analyses. Imazethapyr was measured in two subsamples from each plot sample. Imazethapyr residues were

extracted by shaking 25 g of soil with 100 mL of 0.5 N NaOH for 1 h. Samples were centrifuged for 15 min at 5000 rpm, and 80 mL of the supernatant was decanted. The pH of the supernatant was adjusted to 1.7 with 6 N HCl, 5 g of Celite was added, the contents were stirred, and the mixture was filtered through a 12.5-cm glass fiber filter. The extract was then applied to a MegaBond-Elut C18-OH cartridge (Varian) that had been preconditioned with 5 mL of methanol and 5 mL of Milli-Q water.

Imazethapyr was eluted from the C18-OH cartridge, using 40 mL of 50% methanol/water, onto a Megabond-Elut SCX cartridge (Varian) that had been preconditioned with 5 mL of hexane, 5 mL of methanol, and 5 mL of Milli-Q water. Imazethapyr was eluted from the SCX column using 30 mL of KCl-saturated methanol into a round-bottom flask. One milliliter of Milli-Q water was added to the flask. The sample was evaporated to near dryness and redissolved in 10 mL of pH 2.0 water. The sample was transferred to a separatory funnel to which 25 mL of methylene chloride was added. The sample was shaken for 1 min. The bottom layer was removed and saved. This procedure was repeated twice. One milliliter of Milli-Q water was added, and the sample was evaporated to near dryness and then re-evaporated with 20 mL of methanol. The sample was redissolved in 5 mL of Milli-Q water.

Imazethapyr concentration was determined using a high-performance liquid chromatograph (Hewlett-Packard model 1050) equipped with a UV detector at a wavelength of 254 nm. Liquid chromatography separation was performed on a C8 reversed-phase 250×4.6 mm Zorbax column (Hewlett-Packard) with a mobile phase of acetonitrile/water/formic acid (32:66:2) at a flow rate of 1.00 mL min^{-1} . Sample injection volume was $200 \mu\text{L}$.

A linear calibration curve based on peak area was generated using known imazethapyr concentrations ranging from 0.05 to $1 \mu\text{g mL}^{-1}$. The stock solution of imazethapyr consisted of analytical grade herbicide (chemical purity >99%) dissolved in 1 mL of acetone and diluted with Milli-Q water. The concentration of imazethapyr in extracts from soil samples was determined by entering peak area values into a regression equation describing the calibration curve.

Greenhouse Experiment. Pregerminated imazethapyr-resistant and -susceptible canola crops were seeded at 11 kg ha^{-1} into soil samples taken from limed and unlimed plots. Soil from the three field sampling times, immediately and 9 and 18 weeks after imazethapyr application, was used. Plants were grown in the greenhouse at $25 \pm 2 \text{ }^\circ\text{C}$ with supplemental lighting from Phillips 40 W Agri-grow lights. Canola growth was measured during a 3-week period.

Sorption–Desorption. Soil samples used for sorption–desorption and aged residue studies were a Ves loam taken from the Lamberton Experiment Station in Minnesota. The samples were from long-term variable-pH plots within a single field, and soil sampling depth was 0–16 cm. The pH levels of the soil samples ranged from 5.4 to 7.7, with the OC content ranging from 2.26 to 3.31%, determined as discussed previously.

Sorption was characterized using the batch equilibration technique, using soil freshly spiked with imazethapyr (Chem-Service) at four concentration levels: 1.6, 4.8, 16, and 48 mg kg^{-1} . Each sample also contained 126–148 Bq of ^{14}C -labeled imazethapyr (specific activity = $1.18 \mu\text{Ci mmol}^{-1}$) (American Cyanamid). Triplicate 5-g soil samples were spiked with

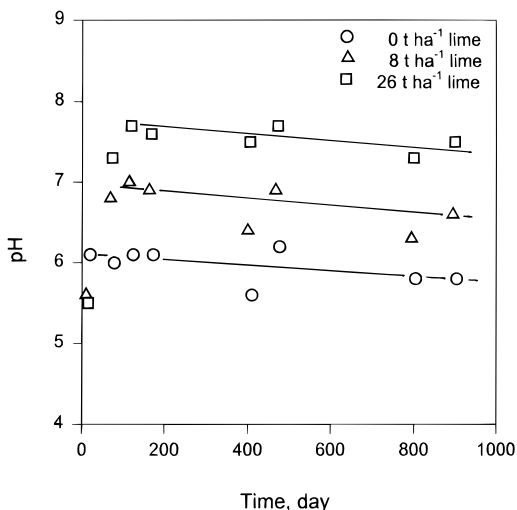


Figure 2. Effect of lime addition on field soil pH.

imazethapyr and then equilibrated with 10 mL of 0.01 N CaCl_2 solution by shaking mechanically at $21 \pm 2^\circ \text{C}$ in 30-mL glass centrifuge tubes, closed with Teflon-lined caps, for 24 h. Previous kinetic studies (data not shown) indicated that equilibrium was reached within 1 h and that no changes in concentration occurred after 48 h of shaking and no degradation occurred within this period. Soils were then centrifuged at 3500 rpm for 45 min, and 4 mL of supernatant was removed for analysis.

Desorption experiments were conducted immediately after the sorption experiment using the soils from all four initial concentrations. After centrifuging in the sorption experiment and removal of 4 mL for analysis, 4 mL of 0.01 N CaCl_2 without chemical was added to the soil. Soils were resuspended in a vortex action shaker and then shaken for another 24 h. Soil suspensions were centrifuged, and 4 mL of supernatant was removed for analysis. This desorption cycle was repeated four times for each sample.

One-milliliter aliquots of the clear supernatants were mixed with 10 mL of EcoLite scintillation cocktail, and the amount of radioactivity was determined by liquid scintillation counting (LSC) for 10 min in a 1500 Tri-Carb Packard liquid scintillation analyzer. The amount of imazethapyr in solution was calculated by considering the specific activity of the chemical.

The amount of chemical sorbed to the soil after equilibration was calculated from the difference between the amount initially added and the equilibrium solution concentration. Sorption and desorption isotherms were calculated using the linearized form of the Freundlich equation: $\log C_s = \log K_f + 1/n_f \log C_e$, where C_s is the amount of chemical sorbed ($\mu\text{g g}^{-1}$ of soil), C_e is the equilibrium concentration ($\mu\text{g mL}^{-1}$ of solution), and K_f and $1/n_f$ are empirical sorption-desorption coefficients. Sorption-desorption coefficients were calculated by the least-squares technique on the mean of the replicates of the log-transformed equilibrium data. K_f and $1/n_f$ standard deviations were calculated. Sorption coefficients were also calculated as a function of OC, $K_{f-oc} = K_f/\% \text{OC} \times 100$.

Sorption-Desorption of Aged Residues. To determine the effect of aging on imazethapyr sorption, soils were spiked at $48 \mu\text{g kg}^{-1}$ imazethapyr, which contained 137 Bq of ^{14}C -labeled imazethapyr. The soils were aged at 25°C in 30-mL centrifuge tubes closed with Teflon-lined caps for 1, 2, 3, and 6 months. After the 3-month sampling, spent lime was added to the half of the remaining 3-month-aged soil samples at an equivalent of 26 t ha^{-1} , and the samples were allowed to continue to age for 3 more months. At each sampling time, 20 mL of 0.01 N CaCl_2 was added to each tube and the tubes were shaken gently on a reciprocating shaker at $21 \pm 2^\circ \text{C}$ for 24 h. The soil/solution ratio and 24-h equilibration were selected to match conditions of the sorption-desorption study. Suspensions were centrifuged at 3500 rpm for 45 min, and the supernatant was transferred to preweighed flasks. One-

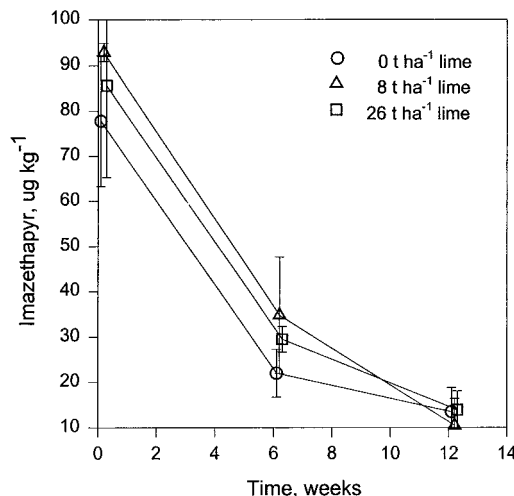


Figure 3. Imazethapyr degradation as a function of liming field to different pH levels.

Table 1. Effect of Imazethapyr and pH on Root Yield, Extractable Sucrose, and Percent Sucrose

year	treatment	applied lime (t ha ⁻¹)	soil pH	root yield (t ha ⁻¹)	extractable sucrose (kg ha ⁻¹)	sucrose (%)
1997	none	0	5.7	32.3	4000	13.9
		8	6.8	50.9	6900	14.6
		26	7.7	48.0	6562	14.7
	imazethapyr	0	5.7	0	0	0
		8	6.8	0	0	0
		26	7.7	0	0	0
	LSD (0.05)			2.5	33	0.3
1998	none	0	5.8	48.0	7955	18.0
		8	6.6	51.8	8861	18.5
		26	7.5	65.7	10749	17.8
	imazethapyr	0	5.8	17.3	2552	16.1
		8	6.6	47.1	7751	17.9
		26	7.5	56.7	9271	17.8
	LSD (0.05)			6.9	2452	5.0

milliliter aliquots were removed for analysis, mixed with 10 mL of EcoLite scintillation cocktail, and the amount of radioactivity was determined by LSC. The remaining supernatant was then processed as discussed under Soil Analyses.

The imazethapyr peak was collected in a scintillation vial, mixed with scintillation cocktail, and quantified by LSC. Imazethapyr was extracted from the soil as previously discussed under Soil Analyses. Sorption coefficients, K_d , were calculated from the amounts of imazethapyr in solution and sorbed to soil at each sampling time.

RESULTS AND DISCUSSION

Field Results. Field plots were limed and imazethapyr applied in 1996. Soil pH increased during the course of the experiment in plots that were limed (Figure 2). Field plot soil pH increased by 1 pH unit in the soil in the field plots limed at 8 t ha^{-1} and by 2 pH units in soil limed at 26 t ha^{-1} and did not significantly change in unlimed plots. The pH was relatively stable over three growing seasons. Imazethapyr concentration decreased rapidly in the surface 15 cm of soil during the 1996 growing season; 80% dissipated within 3 months (Figure 3). There was no effect of pH on the initial dissipation; $\sim 13 \mu\text{g kg}^{-1}$ remained in all three pH soils 3 months after application.

In the imazethapyr-treated plots the year following liming and imazethapyr application (1997), there was sufficient imazethapyr carry-over to affect sugarbeet regardless of pH. In all three pH plots, the sugarbeet germinated and died, resulting in zero yield (Table 1).

Table 2. Imazethapyr and pH Effects on Canola in the Greenhouse

lime (t ha ⁻¹)	pH	canola height (cm)	
		resistant canola	susceptible canola
0	5.7	5.3	0.3
8	6.8	6.1	2.9
26	7.7	6.5	2.8
LSD (0.05)		0.8	0.9

Table 3. Imazethapyr Sorption–Desorption as a Function of pH

pH	K_f (mg ^(1-1/n) kg ⁻¹ L ^{1/n})	$1/n_f$	$1/n_d$	K_{f-oc} (mL g ⁻¹)
7.4	0.57 (0.52–0.62)	1.04 ± 0.10	0.19 ± 0.11	23
6.2	2.07 (2.00–2.14)	0.97 ± 0.01	0.53 ± 0.04	82
5.8	3.07 (2.91–3.24)	0.98 ± 0.02	0.53 ± 0.03	99
5.6	2.76 (2.59–2.95)	1.01 ± 0.01	0.52 ± 0.06	114
5.4	3.55 (3.47–3.63)	1.03 ± 0.02	0.62 ± 0.08	163

^a Standard error about the mean. ^b Values ± standard error.

It is interesting to note that sugarbeet root yield and extractable sucrose were significantly greater in limed soils without imazethapyr application than in unlimed soils, indicating a response of sugarbeet growth and yield to soil pH.

Field 2 was planted to sugarbeet in 1998 (2 years after liming and imazethapyr application). Imazethapyr-treated plots and plots not treated with herbicide had greater sugarbeet root yields and extractable sucrose when lime was used to increase soil pH (Table 1). Plots limed at 26 t ha⁻¹ and treated with imazethapyr produced 40 t ha⁻¹ greater sugarbeet root yield and 6700 kg ha⁻¹ more extractable sucrose than unlimed plots treated with imazethapyr. Imazethapyr-treated plots limed at 8 t ha⁻¹ produced 30 t ha⁻¹ greater sugarbeet root yield and 5200 kg ha⁻¹ more extractable sucrose than unlimed plots treated with imazethapyr. No-herbicide control plots limed at 26 t ha⁻¹ produced 18 t ha⁻¹ greater root yield and 2800 kg ha⁻¹ greater extractable sucrose than unlimed no-herbicide control plots. Limed no-herbicide control plots yielded more extractable sucrose than unlimed imazethapyr-treated plots in all comparisons, but the differences were not significant due to high variability in the experiment. Therefore, 2 years after application, sufficient imazethapyr residues were available in low-pH soils to adversely affect sugarbeet yield.

Greenhouse Results. Greenhouse studies were conducted to determine the bioavailability of the imazethapyr residues to susceptible and imazethapyr-resistant canola in limed and unlimed soils at each field sampling time in 1996 (Table 2). At all pH levels and at all sampling times, imazethapyr affected growth of susceptible canola but did not affect resistant canola. Although the same amount of imazethapyr was present for each pH soil at each sampling time (discussed above), the imazethapyr present was more bioavailable at pH <6 than at pH >6.

Sorption–Desorption. Imazethapyr sorption isotherms fit the Freundlich equation ($r^2 > 0.99$) and were linear ($1/n_f = 1.0$) at soil pH levels from 5.4 to 7.7, indicating that sorption is not dependent on concentration (Table 3). The fact that Freundlich isotherm slopes, $1/n_f$, were not significantly different for all soils allowed comparison of the Freundlich K_f constants as a measure of the extent of sorption for the different soils in the range of concentrations used. Less herbicide was sorbed

Table 4. Percent Imazethapyr Remaining as a Function of Laboratory Incubation Time

pH	imazethapyr remaining (%)			
	1 month	2 months	3 months	6 months
5.4	85 ^a	71	72 ± 4 ^b	58 ± 7
5.8	55 ± 15	69 ± 1	64 ± 9	55 ± 8
7.7	84 ± 3	73 ± 9	72 ± 7	65 ± 4

^a Only one sample. ^b Values ± standard error.

Table 5. Effect of Aging on Imazethapyr Sorption As Affected by Soil pH

pH	K_d at selected times after application (mL g ⁻¹)			
	1 month	2 months	3 months	6 months
5.4	3.2 ^a	2.7	8.2 ± 1.7 ^b	6.1 ± 0.6
5.8	2.4 ± 0.8	2.8 ± 0.1	3.1 ± 1.4	4.9 ± 1.3
7.7	0.7 ± 0.2	1.1 ± 0.9	0.9 ± 0.7	1.3 ± 0.8

^a Only one sample. ^b Values ± standard error.

onto soils with higher pH levels (7.4–7.7) than on low-pH soils, consistent with previous research (Renner et al., 1988; Stougaard et al., 1990; Che et al., 1992). For example, soil with a pH ≥7.4 had K_f values <0.6, whereas for pH 6.2 soil, K_f was 2.1 and for pH 5.4 soil, the K_f value was 3.6 (Table 3). At lower pH levels imazethapyr sorption can also be influenced by soil OC content. K_{f-oc} increased with decreasing pH, similar to what was observed by Oliveira et al. (1999).

Desorption isotherms fit the Freundlich equation ($r^2 > 0.93$), and hysteresis was observed during desorption from all pH soils ($1/n_d < 1/n_f$) (Table 3). Hysteresis was previously observed in various soils (Gan et al., 1994). At higher soil pH levels, greater desorption hysteresis was observed than at low soil pH. This indicates that although there is less imazethapyr sorbed at a high pH, what is sorbed is more resistant to being desorbed from soil, whereas at low pH the imazethapyr is more readily desorbed. For instance, at pH levels of 7.4, $1/n_d < 0.4$, whereas at pH levels <6.2, $1/n_d > 0.5$.

To determine the effect of aging on imazethapyr sorption, imazethapyr was applied to soil, which was allowed to incubate for up to 6 months. During the 6 months, the rates of degradation of imazethapyr were not significantly different for the three pH soils. The amounts of parent imazethapyr herbicide remaining 6 months after application (~60%) were not significantly different among the three soil pH levels (Table 4). As discussed earlier, imazethapyr sorption was not concentration dependent ($1/n_f = 1$); therefore, single-point sorption coefficients (K_d) could be used to compare sorption as a function of pH and time, despite differences in imazethapyr concentrations remaining at each sampling time.

Sorption generally increased as a function of incubation time, and the increase was independent of soil pH (Table 5). For instance, K_d values increased significantly during the 6-month incubation period at the lower pH level of 5.4. At 1 month after application, the remaining imazethapyr had a $K_d = 3.2$, which was about half of that calculated for the remaining imazethapyr at 3–6 months after application. Although not significant, K_d was also greater by a factor of 2 at 6 months compared to at 1 month after application at pH levels 5.8 and 7.7.

It appears that the increase in sorption with aging is, in part, a function of the rate of formation of imazethapyr cation as opposed to changes in sorption mechanism of the neutral species. As previously dis-

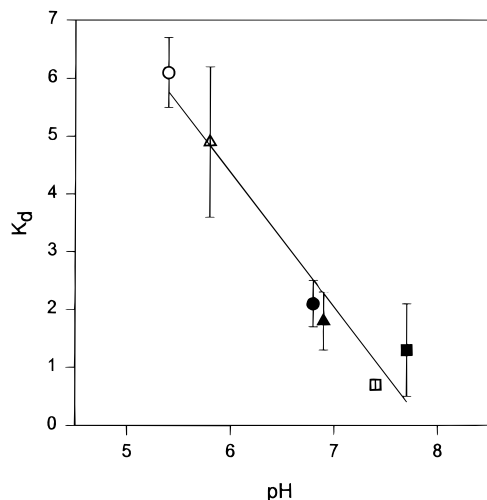


Figure 4. Sorption K_d values of imazethapyr aged in different pH soils for 6 months (open symbols) and K_d values of the same soils to which 26 t ha^{-1} lime was added. Imazethapyr was aged for 3 months and then was aged for another 3 months (solid symbols).

cussed, imazethapyr is an amphoteric molecule; therefore, at any soil pH, cationic, anionic, and molecular species would exist simultaneously. For instance, a soil with a measured bulk pH of 6.1 would have a solution pH at the soil particle surface 2 pH units lower, for example, pH 4.1. Therefore, on the basis of the pK_a for protonation, $\sim 1\%$ of the imazethapyr in solution would be cationic. In low-pH soil there would be greater amounts of cation in solution than in high-pH soil. The cations, once formed, can be sorbed by the soil colloid during the aging period.

The increased sorption as a result of cation formation during aging is a reversible process for imazethapyr. When low-pH soils at 3 months were limed to higher pH levels and incubated for another 3-month period, sorption K_d values decreased to those which would be predicted from the pH- K_d relationship for soils incubated for 6 months (Figure 4). For instance, imazethapyr in pH 5.8 soil aged for 6 months had a $K_d = 4.9$ (open triangle, Figure 4). However, when imazethapyr-treated pH 5.8 soil was aged for 3 months and then limed with 26 t ha^{-1} and aged for 3 more months, the pH increased to 6.8 and the K_d decreased to 1.8 (solid triangle, Figure 4). Therefore, for soils incubated for 3–6 months, imazethapyr sorption can be predicted from pH using the equation $K_d = -2.335\text{pH} + 18.38$, $r^2 = 0.938$. If changes in neutral species sorption were a significant mechanism, we would not have observed the decrease in sorption with the increase in pH.

Conclusions. Although soil pH did not affect imazethapyr persistence in both field and laboratory experiments, it appeared to affect its bioavailability, resulting in carry-over effects on sugarbeet. For instance, although 80% of the applied imazethapyr had dissipated 3 months after application, the remaining residues were more bioavailable at low pH as indicated by greater effects on susceptible canola. Two years after imazethapyr application, the residues at low pH were more bioavailable than at high pH, as indicated by the significantly lower sugarbeet root yield at low pH. Although there was greater imazethapyr sorption at lower pH levels than at the higher pH levels, there was less desorption hysteresis exhibited at lower soil pH levels than at higher soil pH levels, indicating that at low pH, the

imazethapyr was more readily desorbable. It appears that the increase in sorption with aging is in part a function of the rate of formation of imazethapyr cation. In low-pH soil, greater amounts of cation are formed and sorbed by the soil colloid than in high-pH soil during the aging period, a process that is reversible. Raising soil pH with lime would reduce sugarbeet injury from carry-over of imazethapyr but would not totally prevent sugarbeet injury 2 years after application. Results of these experiments also suggest that raising soil pH with lime in soils with a low pH will increase the sugarbeet yield potential of the soils even in the absence of herbicide residue.

ACKNOWLEDGMENT

We thank American Cyanamid for kindly supplying the ^{14}C -labeled imazethapyr.

LITERATURE CITED

- Ball, D. F. Loss-on-ignition as an estimate of organic matter and organic carbon in non-calcareous soils. *J. Soil Sci.* **1964**, *15*, 84–92.
- Boesten, J. J. T. I.; Van der Pas, L. J. T. Test of some aspects of a model for the adsorption/desorption of herbicides in soil. *Aspects Appl. Biol.* **1983**, *4*, 495–501.
- Carruthers, A.; Oldfield, J. F. T. Methods for assessment of beet quality. Part III. Summation of non-sugars. *Int. Sugar J.* **1961**, *63*, 137–139.
- Che, M.; Loux, M. M.; Traina, S. J.; Logan, T. J. Effect of pH on sorption and desorption of imazaquin and imazethapyr on clays and humic acid. *J. Environ. Qual.* **1992**, *21*, 698–703.
- Cox, L.; Koskinen, W. C.; Yen, P. Y. Changes in sorption of imidacloprid with incubation time. *Soil Sci. Soc. Am. J.* **1998**, *62*, 342–347.
- Gan, J.; Weimer, M. R.; Koskinen, W. C.; Buhler, D. D.; Wyse, D. L.; Becker, R. L. Sorption and desorption of imazethapyr and 5-hydroxyimazethapyr in Minnesota soils. *Weed Sci.* **1994**, *42*, 92–97.
- Gee, G. W.; Bauder, J. W. Particle-size analysis. In *Methods of Soil Analysis*, 2nd ed.; Agronomy Monograph 9; Klute, A., et al., Eds.; ASA and SSSA: Madison, WI, 1986; Part 1, pp 383–409.
- Goetz, A. J.; Lavy, T. L.; Gbur, E. E., Jr. Degradation and field persistence of imazethapyr. *Weed Sci.* **1990**, *38*, 421–428.
- Green, R. E. Pesticide-clay-water interactions. In *Pesticide in Soil and Water*; Guenzi, W. D., Ed.; Soil Science Society of America: Madison, WI, 1974; pp 3–37.
- Koskinen, W. C.; Harper, S. S. The retention process: Mechanisms. In *Pesticides in the Soil Environment: Processes, Impacts and Modeling*; Cheng, H. H., Ed.; SSSA Book Series 2; SSSA: Madison, WI, 1990; pp 51–77.
- Loux, M. M.; Reese, K. D. Effect of soil type and pH on persistence and carryover of imidazolinone herbicides. *Weed Technol.* **1993**, *7*, 452–458.
- Loux, M. M.; Liebl, R. A.; Slife, F. W. Availability and persistence and carryover of imidazolinone herbicides. *Weed Technol.* **1989**, *7*, 452–458.
- McCall, P. J.; Agin, G. L. Desorption kinetics of picloram as affected by residence time in the soil. *Environ. Toxicol. Chem.* **1985**, *4*, 37–44.
- Oliveira, R. S., Jr.; Koskinen, W. C.; Ferreira, F. A.; Khakural, B. R.; Mulla, D. J.; Robert, P. C. Spatial variability of sorption/desorption of imazethapyr. *Weed Sci.* **1999**, *47*, 243–248.
- Onofri, A. Biological activity, field persistence and safe re-cropping intervals for imazethapyr and rimsulfuron on a silty-clay soil. *Eur. Weed Res. Soc.* **1996**, *36*, 73–83.

- Pignatello, J. J.; Gerradino, F. J.; Huang, L. Q. Elution of aged and freshly added herbicides from a soil. *Environ. Sci. Technol.* **1993**, *27*, 222–228.
- Renner, K. A.; Meggitt, W. F.; Penner, D. Effect of soil pH on imazaquin and imazethapyr adsorption to soil and phytotoxicity to corn (*Zea mays*). *Weed Sci.* **1988**, *36*, 67–73.
- 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 Science.* **1990**, *38*, 67–73.
- Wepplo, P. J. Chemical and physical properties of the imidazolinones. In *The Imidazolinones Herbicides*; Shaner, D. L.,

O'Connor, S. L., Eds.; CRC Press: Boca Raton, FL, 1991; pp 15–29.

Received for review May 20, 1999. Revised manuscript received February 28, 2000. Accepted March 13, 2000. Mention of a company name or trade name is for information only and does not imply recommendation by the North Dakota State University, USDA-ARS, or University of Minnesota.

JF990543W