

Sorption–Desorption of Aminocyclopyrachlor in Selected Brazilian Soils

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ABSTRACT: Aminocyclopyrachlor sorption/desorption was investigated in 14 soils from Brazil, representing a range of pH, and organic carbon (OC) and clay contents. The Freundlich equation adequately described behavior of aminocyclopyrachlor in soil. Freundlich sorption coefficient (K_f) values ranged from 0.06 to 1.64 and $1/n$ values for ranged from 0.9 to 1.0. Sorption was correlated to OC ($K_{f,oc}$ ranged from 11 to 64) and clay contents. The lowest sorption was found for soils with very low OC contents (0.50–0.65%) and loamy-sand to sand textures. The $1/n$ values for desorption were lower than those observed for sorption, suggesting that aminocyclopyrachlor sorption by soil was not reversible; hysteresis coefficients ranged from 0.13 to 0.74. The results suggest that although aminocyclopyrachlor would be very mobile based on its sorption coefficients, its potential depth of leaching may be overestimated due to the hysteretic desorption.

KEYWORDS: adsorption, hysteresis, pyrimidine carboxylic acids, soil properties, tropical soils

INTRODUCTION

Aminocyclopyrachlor (6-amino-5-chloro-2-cyclopropyl-4-pyrimidincarboxylic acid) (Figure 1) is a new herbicide from a new class of chemistry known as pyrimidine carboxylic acids.^{1,2} In earlier stages, aminocyclopyrachlor was previously developed as DPX-MAT 28 (acid form), or as DPX-KJM44 (methyl ester form).³ Although both compounds are equally active as herbicides, the methyl ester form has lower vapor pressure and is more volatile than the acid form.⁴ Approximately 80% of the methyl ester is converted to the free acid into plants six hours after leaf absorption.³

Aminocyclopyrachlor has been developed for noncrop uses such as bare ground, brush, right-of-way, and turf, as well as for range, pasture and invasive weed control⁵ and has both foliar and soil activity on susceptible species.⁶ It is active on a number of glyphosate and ALS-resistant weeds such as marestail,⁷ Russian thistle, kochia, and prickly lettuce.^{5,8} Other weeds efficiently (80–100%) controlled for periods ranging from 60 days to one year after application are yellow poplar and red oak species,⁹ musk thistle,¹⁰ cogongrass,¹¹ and marestail.⁷ Other species like leafy spurge, Canada thistle, Scotch thistle, Russian knapweed, field bindweed, common milkweed, salt cedar, Russian olive,¹² Russian thistle, pigweeds, marestail, kudzu and volunteer grains⁸ also exhibit excellent control (>90%) one year after treatment. Reports of plant responses to aminocyclopyrachlor include epinasty of newly developing leaves and stems primarily on broadleaf species, indicating that its mode of action, yet not fully known, is consistent with synthetic auxin herbicides.⁴

Aminocyclopyrachlor application rates to date in field research projects have ranged from 35 to 315 g active ingredient per hectare. Most sensitive perennial weeds are well controlled at 70–140 g ha⁻¹.¹² In spite of the low application rates, long periods of residual activity are expected for most proposed uses of aminocyclopyrachlor. Although aminocyclopyrachlor has exhibited a number of positive stewardship attributes with very low

impact to mammals and the environment,⁵ not much is known about its fate in soil. As a result, aspects related to its sorption and desorption from soil are of main interest concerning both its agronomical use and environmental fate. This work was aimed at characterization of sorption and desorption coefficients of aminocyclopyrachlor in a diverse collection of soils from Brazil that have a wide range in soil properties.

MATERIALS AND METHODS

Soils. Fourteen Brazilian soils with varying physicochemical characteristics were selected for this study. Samples were collected from the 0–10 cm depth, air-dried, and ground to pass through a 2 mm sieve. Main physicochemical properties of soils are given in Table 1. Sand and clay contents were determined by the hydrometer method. Soil pH was measured in a 1:2 soil/deionized water mixture. The organic C content was determined by dry combustion at 1,370 °C.

Chemicals. ¹⁴C-Labeled aminocyclopyrachlor and pure analytical standards were graciously provided by DuPont (Wilmington, DE). Four solutions (1.41; 0.47; 0.14 and 0.047 μmol L⁻¹) were prepared in 0.01 N CaCl₂, and ¹⁴C-aminocyclopyrachlor was added to them to give a solution radioactivity of ~109 Bq mL⁻¹. Final solutions contained less than 0.4% methanol and were stored in foil-covered flask at 4 °C in the dark.

Sorption Kinetics. The amount of aminocyclopyrachlor sorbed as a function of time was determined in two diverse soils (BRA1 and BRA4) in order to evaluate the suitability of a 24 h equilibration time in the batch equilibration sorption studies. To 10 g of untreated soil, 10 mL of 0.75 μmol L⁻¹ ¹⁴C-aminocyclopyrachlor solution were added, mixed using a vortex mixer, and shaken on a tabletop shaker. After 0, 2, 4, 8, 24,

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and 48 h, triplicate tubes were removed and centrifuged and 1 mL aliquots were removed for analysis. Five milliliters of scintillation cocktail (EcoLyte, cocktail, ICN Biomedicals, Costa Mesa, CA) was added to the 1 mL aliquot, and the amount of ^{14}C -aminocyclopyrachlor was determined by liquid scintillation counting with a Packard 1500 counter (Packard Instruments, Downer Grove, IL.).

Sorption. Sorption studies were performed using the batch equilibration method. To 10 g of soil in 35 mL glass centrifuge tubes with Teflon-lined caps, 10 mL of aminocyclopyrachlor solution was added. The tubes were thoroughly mixed using a vortex mixer (30 s) and then mechanically shaken on a tabletop shaker at $20 \pm 2^\circ\text{C}$ for 24 h. The tubes were then centrifuged for 20 min at 370g. A 3 mL aliquot was removed using a disposable glass pipet. A 1 mL subsample of the supernatant was analyzed for ^{14}C as discussed above. The amount of chemical sorbed to soil was calculated as the difference in aminocyclopyrachlor concentration in the added solution and in the supernatant after equilibration. All studies were performed in triplicate. No sorption was observed in a blank tube containing solution without soil. Data were fit to the Freundlich equation described below to obtain sorption coefficients.

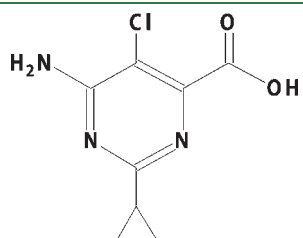


Figure 1. Main physicochemical properties of aminocyclopyrachlor.^{21,23}

Table 1. Physicochemical Properties of Soils

soil	origin (city, state, geographic coordinates)	soil classification ^a	pH H ₂ O	%				clay mineralogy ^c	
				OC	sand	clay	text. ^b	major	minor
BRA1	Marialva, PR (S 23° 31' 21"; W 51° 50' 20")	Oxisol–Rhodic Hapludox (Latossolo Vermelho distrófico)	6.0	1.60	27	65	C	K, H, 2:1	Gib, MgH, An, Go, Qz, VHE
BRA2	Umuarama, PR (S 23° 47' 24"; W 53° 15' 30")	Ultisol (Argissolo Vermelho distrófico)	5.1	0.68	89	7	S	K, H, 2:1	Gib, Go, MgH, An, VHE
BRA3	Pres. Castelo Branco, PR (S 23° 14' 08"; W 52° 10' 09")	Oxisol–Typic Hapludox (Latossolo Vermelho distrófico)	5.4	0.50	88	10	LS	K, H, 2:1, Gib	Go, MgH, An, Qz
BRA4	Umuarama, PR (S 23° 47' 39"; W 53° 15' 02")	Oxisol–Typic Hapludox (Latossolo Vermelho distrófico)	4.9	1.02	85	11	LS	K, H, 2:1, Gib	Go, MgH, An, Qz
BRA5	Mamborê, PR (S 24° 16' 00"; W 52° 30' 00")	Oxisol–Rhodic Hapludox (Latossolo Vermelho distrófico)	5.7	1.83	35	56	C	K, H, 2:1 Gib	VHE, An, MgH
BRA6	Santa Mônica, PR (S 23° 13' 21"; W 53° 05' 05")	Plintisol (Plintossolo Háplico)	5.7	0.90	60	17	SL	K, H, 2:1	Gib, Go, MgH, An, VHE
BRA7	Vilhena, RO (S 12° 46' 54"; W 60° 05' 31")	Oxisol–Rhodic hapludox (Latossolo Vermelho distrófico)	5.9	2.05	38	57	C	K, H, Gib	Go, Qz
BRA8	Rio Verde, GO (S 17° 47' 17"; W 50° 57' 42")	Oxisol–Rhodic hapludox (Latossolo Vermelho distrófico)	6.2	2.17	39	59	C	K, H, Gib	VHE
BRA9	Rondonópolis, MT (S 16° 50' 53"; W 54° 03' 02")	Typic quartzipsaments (Neossolo Quartzarênico órtico)	7.2	0.65	93	5	S	K, Go	Qz
BRA10	Rondonópolis, MT (S 16° 52' 17"; W 53° 50' 17")	Oxisol–Typic Hapludox (Latossolo Vermelho distrófico)	6.1	1.79	45	50	C	K, H, Gib	Go
BRA11	Santa Maria, RS (S 29° 43' 18"; W 53° 43' 31")	Arenic albaqualfs (Planossolo Háplico eutrófico)	6.0	1.06	62	17	SL	K, 2:1	VHE, Qz
BRA12	Barra do Bugres, MT (S 15° 06' 43"; W 57° 18' 09")	Typic quartzipsaments (Neossolo Quartzarênico órtico)	6.5	0.61	92	7	S	K, Go	H, Qz
BRA13	Tangará da Serra, MT (S 14° 39' 01"; W 57° 25' 54")	Oxisol–Typic Hapludox (Latossolo Vermelho distrófico)	5.2	1.63	39	57	C	K, H, Gib	Go, An
BRA14	Barreiras, BA (S 12° 09' 26"; W 45° 27' 13")	Oxisol–Typic Hapludox (Latossolo Vermelho-amarelo)	6.5	0.64	87	11	LS	K	Go, H, An

^a According to Soil Taxonomy and Brazilian Soil Science Society. ^b Texture: C, clay; S, sand; SL, sandy loam; LS, loamy-sand. ^c K = kaolinite; H = hematite; Gib = gibbsite; Go = goethite; VHE = vermiculite with Al-hydroxy interlayer; An = anatasio; Qz = quartz; MgH = maghemite; 2:1 = smectites and or vermiculites.

Desorption. Desorption was determined for aminocyclopyrachlor at two concentrations (1.41 and $0.047 \mu\text{mol L}^{-1}$) on all 14 soils. Desorption was determined immediately after sorption by replacing the 3 mL aliquot removed with the same volume of 0.01 N CaCl_2 . The tubes were then mixed using a vortex mixer, shaken for 24 h, centrifuged, and the supernatant analyzed as previously described and replaced again. This was done for three desorption steps. All studies were done in triplicate.

Sorption and Desorption Model. Sorption coefficients K_f and $1/n$ were calculated from the slope and intercept of the log form of the Freundlich equation: $\text{Log} [C_s] = \text{log } K_f + 1/n \text{ log } [C_e]$; where $[C_s]$ is the concentration ($\mu\text{mol kg}^{-1}$) of aminocyclopyrachlor sorbed onto soil after equilibration and $[C_e]$ is the aminocyclopyrachlor concentration ($\mu\text{mol L}^{-1}$) after equilibration. Sorption distribution coefficients ($K_d \text{ L kg}^{-1}$, where $K_d = [C_s]/[C_e]$), and $K_{oc} \text{ L kg}^{-1}$, where $K_{oc} = (K_d/(\% \text{ OC})) \times 100$) were also calculated. Desorption K_f and $1/n$ were determined similarly to the sorption coefficients, from a plot of amount of remaining chemical sorbed at each desorption step versus the equilibrium concentration. The desorption K_d value for the third desorption step was also calculated for comparison to the sorption K_d . The hysteresis coefficient, H , for the sorption–desorption isotherms was calculated according to the formula $H = (1/n_{\text{desorption}})/(1/n_{\text{sorption}})$, where $1/n_{\text{sorption}}$ and $1/n_{\text{desorption}}$ are the Freundlich slopes obtained for the sorption and desorption isotherms, respectively.¹³

RESULTS AND DISCUSSION

Sorption Kinetics. The results from the study on the rate of sorption of aminocyclopyrachlor in soils BRA1 and BRA4 (Figure 2) showed that >50% of the total herbicide sorbed at 48 h was accomplished immediately after solution contact with

both soils, increasing to 95–100% after 24 h. For most herbicides, faster initial sorption reflects the sorption on the most accessible sites, whereas the slower sorption (between 8 and 24 h) reflects sorption on less accessible sites. While slower sorption may

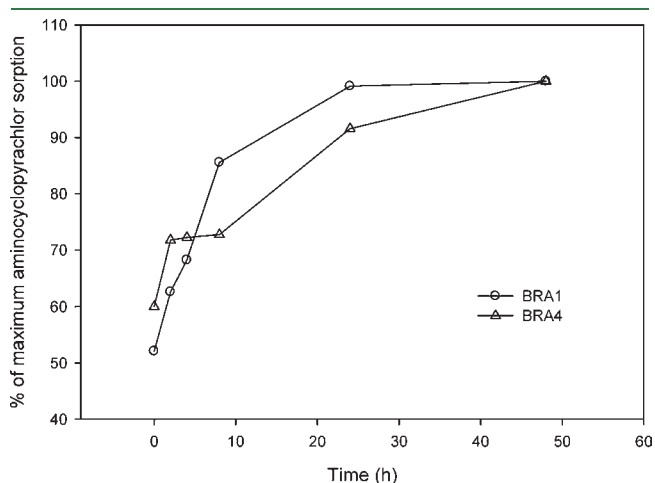


Figure 2. Sorption kinetics of aminocyclopyrachlor in soils BRA1 and BRA4. Each point is the mean of three replicates.

have a physical origin corresponding to diffusion of the herbicide into soil organic matter for some pesticides^{14,15} it may not be the case for BRA4, which has lower OC and clay contents and a lower pH as compared to BRA1. Our results are consistent with fast sorption kinetics of other weak acid herbicides such as 2,4-D, picloram, and aminopyralid.^{16,17} Thus, a 24 h period was considered suitable for attaining operational equilibrium.

Sorption. Aminocyclopyrachlor Freundlich sorption parameters are presented in Table 2. The Freundlich equation adequately described ($R^2 \geq 0.98$) the behavior of aminocyclopyrachlor for all soils. Because sorption was not concentration-dependent, $1/n$ sorption values were ~ 1.0 (Table 2) and not significantly different from each other; K_f values can be compared between soils. In general, K_f values were low in general and ranged from 0.06 (BRA3) to $1.16 \mu\text{mol}^{(1-1/n)} \text{L}^{1/n} \text{kg}^{-1}$ (BRA7) (Table 2, Figure 3).

Significant linear correlations ($P < 0.05$) indicated that OC ($r = 0.88$) and clay contents ($r = 0.84$) are positively correlated to aminocyclopyrachlor Freundlich sorption coefficients. Linear equations that described K_f as a function of carbon contents ($K_f = -0.1867 + 0.5250\% \text{ OC}$, $R^2 = 0.76$) or as a function of clay contents ($K_f = 0.07642 + 0.01237\% \text{ clay}$, $R^2 = 0.71$) were slightly worse predictors of K_f when compared to multiple regression fit for both soil properties ($K_f = -0.141 + 0.418\% \text{ OC} + 0.0028\% \text{ clay}$, $R^2 = 0.77$).

Table 2. Freundlich sorption parameters for aminocyclopyrachlor in different soils from Brazil

soil	$\mu\text{mol}^{(1-1/n)} \text{L}^{1/n} \text{kg}^{-1}$		$1/n$ sorption	R^2	init concn desorption ($\mu\text{mol L}^{-1}$)	$1/n$ desorption	R^2	H
	K_f	$K_{f,oc}$						
BRA1	0.63 (0.61–0.64) ^a	39 (38–40)	0.97 ± 0.01	0.9997	1.41 0.047	0.21 0.21	0.9703 0.9778	0.22 0.22
BRA2	0.22 (0.20–0.23)	32 (30–34)	0.94 ± 0.04	0.9968	1.41 0.047	0.24 0.20	0.7157 0.8235	0.13 0.21
BRA3	0.06 (0.05–0.06)	11 (10–13)	0.90 ± 0.06	0.9913	1.41 0.047	0.24 0.28	0.8374 0.8359	0.27 0.32
BRA4	0.34 (0.32–0.36)	33 (31–35)	0.95 ± 0.03	0.9982	1.41 0.047	0.33 0.38	0.9673 0.9955	0.35 0.40
BRA5	0.52 (0.48–0.57)	28 (26–31)	0.97 ± 0.04	0.9966	1.41 0.047	0.25 0.24	0.9427 0.9731	0.26 0.25
BRA6	0.29 (0.27–0.30)	32 (30–34)	0.99 ± 0.03	0.9984	1.41 0.047	0.65 0.56	0.9944 0.9935	0.65 0.56
BRA7	1.16 (1.08–1.24)	56 (53–60)	1.01 ± 0.03	0.9985	1.41 0.047	0.38 0.29	0.9009 0.8768	0.37 0.29
BRA8	0.83 (0.83–0.83)	38 (38–38)	1.00 ± 0.01	0.9998	1.41 0.047	0.41 0.36	0.9999 0.8589	0.41 0.36
BRA9	0.07 (0.06–0.08)	11 (9–13)	0.93 ± 0.09	0.9829	1.41 0.047	0.29 0.34	0.7391 0.9724	0.18 0.38
BRA10	0.49 (0.48–0.49)	27 (27–28)	0.98 ± 0.01	0.9999	1.41 0.047	0.44 0.43	0.9849 0.9982	0.44 0.44
BRA11	0.50 (0.48–0.52)	47 (45–49)	0.99 ± 0.02	0.9994	1.41 0.047	0.45 0.41	0.9413 0.9171	0.45 0.41
BRA12	0.09 (0.08–0.10)	15 (13–16)	0.97 ± 0.05	0.9945	1.41 0.047	0.30 0.35	0.9621 0.9348	0.31 0.35
BRA13	1.05 (1.01–1.08)	64 (62–66)	0.99 ± 0.01	0.9997	1.41 0.047	0.47 0.50	0.9770 0.9970	0.47 0.50
BRA14	0.14 (0.13–0.15)	22 (20–23)	1.03 ± 0.04	0.9962	1.41 0.047	0.63 0.43	0.9743 0.7328	0.62 0.42

^a Number in parentheses are confidence intervals (K_f , $K_{f,oc}$) or standard deviation of the mean ($1/n$).

Although aminocyclopyrachlor is a weak acid, no significant correlation was found between K_f and soil pH, which ranged from 4.9 to 7.2. Other auxin-type herbicides, such as pyridine carboxylic acids (picloram), benzoic acids (dicamba), phenoxycarboxylic acids

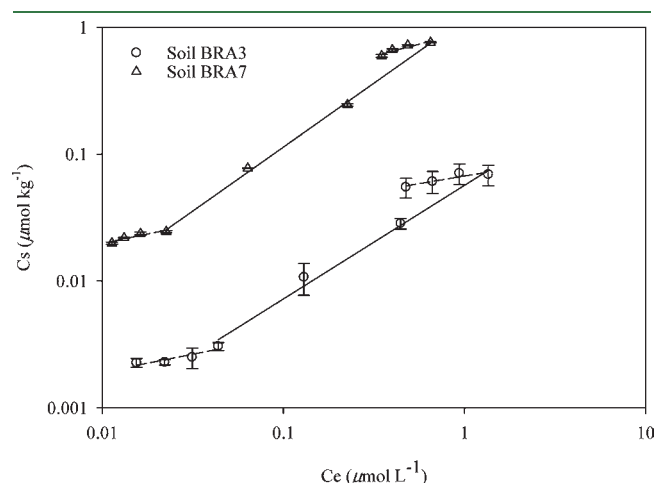


Figure 3. Freundlich isotherm fit to describe aminocyclopyrachlor sorption (solid line) and desorption (dashed line) at concentrations of 1.41 and 0.047 $\mu\text{mol L}^{-1}$ for soils BRA3 and BRA7. Bars associated with each symbol represent the standard deviation of each mean value.

(2,4-D) and quinoline carboxylic acids (quinclorac), usually have their sorption to soil positively correlated to organic carbon, although pH is considered to be the primary soil property influencing sorption.^{18–20} However, it is not unusual to find reports of absence of correlation between sorption coefficients of these herbicides and pH.¹⁷ The absence of significant correlations between K_f and pH in this study could be the result either of the narrow range of pH values of the majority of the soils (9 of the 14 soils had a pH of 5.7 to 6.5) or because all soils had pH values above pK_a of aminocyclopyrachlor (pH of 10 of the 14 soils was >1 unit above the pK_a of 4.65 (21)). At pH levels above the pK_a , weak acid herbicides such as aminocyclopyrachlor are substantially dissociated and not sorbed in most soils. Based on the pK_a of aminocyclopyrachlor, low sorption should be expected for most soils in this study.

Although no correlation could be found between sorption and pH for all soils, when soils with similar OC contents (>1.6% OC) are compared (for instance, BRA7 versus BRA8; BRA5 versus BRA10 or BRA1 versus BRA13), those with the lowest pH have the highest K_f . For low OC soils (<0.7% OC) (for instance, BRA2, BRA9, BRA12 and BRA14) a negative correlation was found between soil pH and K_f ($r = -0.94$, $P < 0.05$). The relationship is valid for the whole range of clay:OC ratio (8–41) of soils in this study. On the other hand, by comparing K_f values for soils with similar clay contents (for instance, BRA2 versus BRA12; BRA4 versus BRA14; BRA6 versus BRA11; or BRA5,

Table 3. Distribution Coefficients (K_d), Sorption Coefficient (K_{oc}), and Desorption K_d for Selected Soils from Brazil

soil	init concn ($\mu\text{mol L}^{-1}$)	sorption K_d (L kg^{-1})	K_{oc}^a (L kg^{-1})	desorption ₃ K_d^b (L kg^{-1})
BRA1	1.41	0.62 ± 0.03^c	39	1.19 ± 0.02
	0.047	0.67 ± 0.02	42	1.34 ± 0.01
BRA2	1.41	0.23 ± 0.03	32	0.48 ± 0.08
	0.047	0.26 ± 0.02	39	0.58 ± 0.03
BRA3	1.41	0.05 ± 0.01	10	0.12 ± 0.03
	0.047	0.07 ± 0.01	14	0.15 ± 0.02
BRA4	1.41	0.34 ± 0.02	33	0.60 ± 0.01
	0.047	0.39 ± 0.03	38	0.66 ± 0.02
BRA5	1.41	0.50 ± 0.01	27	0.93 ± 0.03
	0.047	0.53 ± 0.01	29	1.02 ± 0.07
BRA6	1.41	0.29 ± 0.03	32	0.38 ± 0.05
	0.047	0.28 ± 0.01	32	0.41 ± 0.03
BRA7	1.41	1.17 ± 0.03	57	1.71 ± 0.11
	0.047	1.09 ± 0.04	53	1.76 ± 0.12
BRA8	1.41	0.85 ± 0.05	39	1.28 ± 0.03
	0.047	0.85 ± 0.00	39	1.33 ± 0.02
BRA9	1.41	0.06 ± 0.00	9	0.13 ± 0.03
	0.047	0.07 ± 0.02	11	0.14 ± 0.03
BRA10	1.41	0.48 ± 0.03	27	0.76 ± 0.04
	0.047	0.51 ± 0.02	29	0.81 ± 0.06
BRA11	1.41	0.50 ± 0.00	47	0.75 ± 0.04
	0.047	0.51 ± 0.04	48	0.78 ± 0.03
BRA12	1.41	0.09 ± 0.01	16	0.19 ± 0.02
	0.047	0.09 ± 0.01	15	0.18 ± 0.03
BRA13	1.41	1.07 ± 0.05	66	1.46 ± 0.03
	0.047	1.09 ± 0.01	67	1.47 ± 0.03
BRA14	1.41	0.14 ± 0.01	22	0.21 ± 0.01
	0.047	0.12 ± 0.01	19	0.22 ± 0.01

^a $K_{oc} = K_d / (\% \text{ OC}) \times 100$. ^b Desorption K_d calculated after the third desorption step. ^c Mean K_d value \pm standard deviation of the mean.

BRA7, BRA8 and BRA13), more sorption is found for lower pH soils only if the clay:OC ratio is very low (≤ 17).

As previously mentioned, aminocyclopyrachlor sorption was positively correlated to soil OC content. The range of K_f values varied by a factor of ~ 20 , whereas $K_{f,oc}$ varied by a factor of ~ 6 . $K_{f,oc}$ ranged from 11 (BRA3) to 64 (BRA13). Therefore, although $K_{f,oc}$ reduces variability of sorption coefficient, the effect of normalization to soil organic carbon exhibited a smaller effect than would be expected if organic carbon was the main soil property responsible for sorption. That could reflect the importance of clay contents, as previously discussed, or multiple interaction effects.

Desorption. The range of values for $1/n$ desorption was from 0.20 to 0.65, with most values < 0.50 (Table 2). Figure 3 shows the aminocyclopyrachlor desorption isotherms in soils BRA7 and BRA3 at highest and lowest concentrations in this study.

The $1/n$ values for desorption are much lower than those observed for sorption; hysteresis coefficients, H , ranged from 0.13 to 0.69 (at $1.41 \mu\text{mol L}^{-1}$), and from 0.21 to 0.74 (at $0.047 \mu\text{mol L}^{-1}$). There was no correlation between H and K_f for these soils. These data suggest that once aminocyclopyrachlor was sorbed, it did not readily desorb. No correlations were found between H and soil properties. Hysteresis may be a kinetic effect or an experimental artifact.²² It may also be that a portion of the applied herbicide is very strongly or irreversibly bound to soil. Regardless of the mechanism, hysteresis can impact predicted mobility; desorption K_d coefficients were consistently higher than sorption K_d for all soils and both concentrations (Table 3).

The results suggest that aminocyclopyrachlor would be very mobile based on its sorption coefficients. However, if transport models used sorption K_d values to predict movement, its depth of leaching may be overestimated due to the hysteretic desorption. The average K_d for the third desorption step was a factor of 1.8 times greater than the sorption K_d . These data are the first published data on aminocyclopyrachlor sorption–desorption in soil. However, to better evaluate potential mobility, information is needed on aminocyclopyrachlor degradation and sorption of aged residues.

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REFERENCES

(1) Clark, D. A.; Finkelstein, B. L.; Armel, G. R.; Wittenbach, V. A. *Herbicidal pyrimidines*. U.S. Patent WO/2005/063721, 2005. Available

in <http://www.wipo.int/pctdb/en/wo.jsp?WO=2005063721&IA=US2004042302&DISPLAY=STATUS>.

(2) Finkelstein, B. L.; Armel, G. R.; Bolgunas, S. A.; Clark, D. A.; Claus, J. S.; Crosswicks, R. J.; Hirata, C. M.; Hollingshaus, G. J.; Koeppe, M. K.; Rardon, P. L.; Wittenbach, V. A.; Woodward, M. D. *Proceedings of the 236th ACS National Meeting*; American Chemical Society: Washington, DC, 2008; AGRO No. 19.

(3) Bukun, B.; Bradley Lindenmayer, R.; Nissen, S. J.; Westra, P.; Shaner, D. L.; Brunk, G. Absorption and translocation of aminocyclopyrachlor and aminocyclopyrachlor-methyl ester in Canada Thistle (*Cirsium arvense*). *Weed Sci.* **2010**, *58*, 96–102.

(4) Strachan, S. D.; Casini, M. S.; Heldreth, K. M.; Scocas, J. A.; Nissen, S. J.; Bukun, B.; Bradley Lindenmayer, R.; Shaner, D.; Westra, P.; Brunk, G. Vapor movement of synthetic auxin herbicides: aminocyclopyrachlor, aminocyclopyrachlor-methyl ester, dicamba, and aminopyralid. *Weed Sci.* **2010**, *58*, 103–108.

(5) Claus, J. S.; Holliday, M. J.; Turner, R. G.; Meredith, J. H.; Stephen Williams, C. Aminocyclopyrachlor development and registration update. *North Central Weed Sci. Soc. Proc.* **2009**, *64*, 128.

(6) Rick, S. K.; Turner, R. G.; Meredith, J. H. Biology review of aminocyclopyrachlor. *North Central Weed Sci. Soc. Proc.* **2008**, *63*, 202.

(7) University of Kentucky. College of Agriculture. Department of Plant and Soil Sciences. *Aminocyclopyrachlor (KJM44) combinations for total vegetation and marestail (Conyza canadensis) control. Research summary*. 2008. Available at <http://www.ca.uky.edu/pss/weeds/ivm/pdf/Aminocyclopyrachlor%20for%20Marestail%20and%20Total%20Vegetation%20Contr.pdf>.

(8) Turner, R. G.; Pitts, J. R.; Ganske, D. D.; Hidalgo, E.; Claus, J. S. Aminocyclopyrachlor blend products for vegetation management on railroad and utility sites. *Proc. Soc. Range Manage. Proc. Meet.* **2010**. Available at <https://srm.conference-services.net/reports/template/onetextabstract.xml?xsl=template/onetextabstract.xsl&conferenceID=1756&abstractID=344768>.

(9) Roten, R. L.; Richardson, R. J.; Gardner, A. P. Responses of selected woody plants to DPX-KJM44. *Weed Sci. Soc. Meet. Proc.* **2009**, Abstract 418.

(10) Evans, C. C.; Montgomery, D. P.; Martin, D. L. Musk thistle control on Oklahoma highway rights-of-way with DPX-KJM44. *Weed Sci. Soc. Meet. Proc.* **2009**, Abstract 420.

(11) Wright, R. S.; Byrd, J. D. Potential new herbicides to add to Mississippi Department of Transportation's approved product list. *Weed Sci. Soc. Meet. Proc.* **2009**, Abstract 425.

(12) Westra, P.; Nissen, S.; Gaines, T.; Bekun, B.; Lindenmayer, B.; Shaner, D. Aminocyclopyrachlor for invasive weed management and restoration grass safety in the central great plains. *Proc. North Central Weed Sci. Soc.* **2008**, *63*, 203.

(13) Barriuso, E.; Laird, D. A.; Koskinen, W. C.; Dowdy, R. H. Atrazine desorption from smectites. *Soil Sci. Soc. Am. J.* **1994**, *58*, 1632–1638.

(14) Brusseau, M. L.; Jessup, R. E.; Rao, P. S. C. Nonequilibrium sorption of organic chemicals: elucidation of rate-limit process. *Environ. Sci. Technol.* **1991**, *25*, 134–142.

(15) Pignatello, J. J.; Xing, B. Mechanisms of slow sorption of organic chemicals to natural particles. *Environ. Sci. Technol.* **1996**, *30*, 1–11.

(16) Lu, J.; Wu, L.; Letey, J.; Farmer, W. J. Anionic polyacrylamide effects on soil sorption and desorption of metolachlor, atrazine, 2,4-D and picloram. *J. Environ. Qual.* **2002**, *31*, 1226–1233.

(17) Fast, B. J.; Ferrel, J. A.; MacDonald, G. E.; Jason-Krutz, L.; Kline, W. N. Picloram and aminopyralid sorption to soil and clay minerals. *Weed Sci.* **2010**, *58*, 484–489.

(18) Spadotto, C. A.; Hornsby, A. G. Soil sorption of acidic pesticides: modeling pH effects. *J. Environ. Qual.* **2003**, *32*, 949–956.

(19) Williams, W.; Wehtje, G.; Walker, R. W. Quinclorac: soil behavior and foliar vs. root absorption by torpedograss (*Panicum repens*). *Weed Technol.* **2004**, *18*, 623–633.

(20) Kah, M.; Brown, C. D. Prediction of the adsorption of ionizable pesticides in soils. *J. Agric. Food Chem.* **2007**, *55*, 2312–2322.

- (21) Ryman, J.; Miller, J. S.; Morton, T. Aminocyclopyrachlor: Human Health Risk Assessment for Proposed Uses as Herbicide. March 17, 2010. USEPA Office of Prevention, Pesticides and Toxic Substances. **2010**
- (22) Wauchope, R. D.; Yeh, S.; Linders, J. B. H. J.; Kloskowski, R.; Tanaka, K.; Rubin, B.; Katayama, A.; Kördel, W.; Gerstl, Z.; Lane, M.; Unsworth, J. B. Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. *Pest Manage. Sci.* **2002**, *58*, 419–445.
- (23) DuPont. DPX-MAT28 herbicide technical bulletin. 2009. 7 pp.