

Factors Controlling Sorption of Prosulfuron by Variable-Charge Soils and Model Sorbents

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ABSTRACT

Prosulfuron [1-(4-methoxy-6-methyltriazin-2-yl)-3-[2-(3,3,3-trifluoropropyl) phenylsulfonyl]-urea], a relatively new sulfonylurea herbicide, is a weak acid (pK_a 3.76), and therefore, will undergo pH-dependent speciation and sorption. Understanding prosulfuron sorption in soils is important for predicting its environmental fate. Soil and solution factors controlling sorption were investigated by measuring prosulfuron sorption on five model sorbents (amorphous silica, α -alumina, CaSWy1 montmorillonite, commercial humic acid, and anion exchange resin) and 10 variable-charge soils from $CaCl_2$ and $Ca(H_2PO_4)_2$ solutions as a function of pH and ionic strength. Anion exchange of prosulfuron accounted for up to 82% of overall sorption in the pH range from 3 to 7. The relative importance of anion exchange to prosulfuron sorption was positively correlated to the ratio of anion and cation exchange capacities. Comparison between organic carbon (OC)-normalized sorption (K_{oc}) versus pH for humic acid and variable-charge soils show similar trends with sorption decreasing with increasing pH. However, K_{oc} values estimated from variable-charge soils in the lower pH range where anion exchange has the greatest contribution to sorption was almost one log unit greater than that estimated from humic acid clearly exemplifying the impact of anion exchange. Similarity in K_{oc} -pH curves for humic acid and variable-charge soils may result from the fact that (i) cation exchange capacity increases with increasing OC content, thus effective anion exchange capacity is reduced; and (ii) the relative contribution of hydrophobic and hydrophilic sorption mechanisms was fairly constant. Given that both hydrophilic and hydrophobic sorption of prosulfuron decrease with increasing pH, addition of fertilizer and lime amendments may enhance the potential for off-site leaching of recently applied acidic pesticides.

SULFONYLUREA HERBICIDES are popular worldwide because of their environmentally friendly characteristics such as high herbicidal activity at a low application rate and low mammalian toxicity. Prosulfuron, a weak acid with a pK_a of 3.76, is a relatively new sulfonylurea herbicide, registered in USA for corn in late 1990s for use in grass and weed control. Although sulfonylureas are effective at low application rates (10–40 g of active ingredient ha^{-1}) and dissipate rapidly in soils through hydrolysis reactions (Weed Science Society of America, 2002), off-site transport of sulfonylurea sorbed to airborne soil particles has been shown to negatively affect nontarget biota (Fletcher et al., 1993).

Several dissipation studies of sulfonylurea herbicides have been conducted in aqueous solutions (Bray et al., 1997; Dinelli et al., 1997), with soils (Sarmah and Saba-

die, 2002; Ukrainczyk and Ajwa, 1996), with pure minerals (Pantani et al., 1994; Ukrainczyk and Ajwa, 1996), and with consideration of microbial activity (Cambon et al., 1992; Hultgren et al., 2002; Joshi et al., 1985; Kulowski et al., 1997; Menniti et al., 2003). The most common transformation process affecting sulfonylureas in solution is the acid- (pH < 6) or base-catalyzed (pH > 10) hydrolytic cleavage of the sulfonylurea bridge. This bridge is susceptible to nucleophilic attack by water molecules on the carbonyl carbon. Sulfonylureas remain fairly stable in neutral pH solutions (Sarmah and Sabadie, 2002). The major hydrolysis products of prosulfuron were identified by Bray et al. (1997) as phenyl sulfonylamide and amino triazine. However, additional metabolites reported for soil-water systems include dimethyl prosulfuron (Hultgren et al., 2002) and sulfonic acid (Menniti et al., 2003), which is probably a subsequent metabolite of dimethyl prosulfuron.

Little has been published on the sorptive behavior of prosulfuron. Most sorption studies on sulfonylurea herbicides have focused primarily on chlorsulfuron, nicosulfuron, and primisulfuron. Several chlorsulfuron sorption studies have demonstrated a positive correlation between sorption and soil organic carbon (OC) content, and/or a negative correlation with soil pH, indicating that chlorsulfuron sorption is favored by hydrophobic interaction between the neutral species and organic soil domains (Beckie and Mc Kercher, 1990; Mersie and Foy, 1986; Walker et al., 1989). However, anion exchange, hydrogen bonding, and charge transfer mechanisms have been shown to be significant for sorption by aluminum and iron oxides, clay minerals, humic acid, and anion exchange resins (Shea, 1986; Borggaard and Streibig, 1988). For variable-charge minerals, Borggaard and Streibig (1989) observed chlorsulfuron sorption to be positively correlated with extractable Al and Fe oxide content as well as soil OC content in the range of 0.1 to 1.58%. For primisulfuron sorption, sorption was correlated with extractable Fe for lower OC soils (<1%), but not in high OC soils (>15%). For permanently negatively charged minerals such as montmorillonite, chlorsulfuron and primisulfuron sorption was negligible, which was attributed to repulsion between the permanent negative charge on the mineral surface and the sulfonylurea anions (Shea, 1986; Borggaard and Streibig, 1988; Ukrainczyk and Ajwa, 1996).

Sorption studies on other sulfonylurea herbicides indicate that entropy-driven hydrophobic sorption to OC, sorption to oxides (anion exchange and hydrogen bonding), and pH must be considered when estimating pro-

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Abbreviations: AEC, anion exchange capacity; CaSWy1, a type of montmorillonite; CEC, cation exchange capacity; HA, humic acid; OC, organic carbon; PZNC, point of zero net charge; QA-52, a type of anion exchange resin.

sulfuron sorption by variable-charge soils. The objective of this study was to quantify the relative contribution of hydrophilic and hydrophobic sorption of prosulfuron by interpreting sorption data collected from various soils and model sorbents as a function of pH, ionic composition, and soil surface charge properties.

MATERIALS AND METHODS

Model Sorbents

Amorphous silica (SiO₂), α -alumina (Al₂O₃), anion exchange resin (QA-52), montmorillonite (CaSWy1), and humic acid (HA) were used as model sorbents. Amorphous silica (0.5–10 μ m) with purity of 99.0% and humic acid with carbon content of 38.28% were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI). Chromatographic-grade alumina (74–150 μ m) with purity of >99.9% was purchased from Fisher Scientific (Hampton, NH). The surface charge of silica and alumina are pH-dependent. Silica with a low point of zero net charge (PZNC) of 2 to 3 (Sposito, 1989) is dominantly negatively charged within the pH range investigated, while alumina with a high PZNC of 6.5 to 9.1 (Goyno et al., 2002; Yopps and Fuerstenau, 1964) is positively charged because of high a PZNC. Quaternary ammonium cellulose anion exchange resin (QA-52) was obtained from Whatman International Ltd. (Maidstone, UK). Montmorillonite was supplied by the Source Clays Repository of the Clay Minerals Society (Aurora, CO). The homoionic <2- μ m Ca-smectite fraction was collected by centrifugation and saturated with Ca²⁺ by five successive equilibrations with 1 M CaCl₂ solution. The clay suspension was then dialyzed and freeze-dried. The QA-52 and CaSWy1 have fairly constant anion and cation exchange capacities (AEC and CEC, respectively) with 103 cmol kg⁻¹ reported for QA-52 and 76.4 cmol kg⁻¹ for CaSWy1 (Van Olphen and Fripiat, 1979).

Soils

Four highly weathered subsurface Oxisols (A1, A2, A3, and DRC) collected from Brazil, three subsurface Andisols (K1, K2, and K3) from South Korea, two weathered surface Ultisols (4R and 8R) from Costa Rica, and one moderately weathered surface Alfisol (Toronto series, fine-silty, mixed, superactive, mesic Udollic Epiaqualfs) from Indiana, USA, were used. Subsurface samples were collected at the depth of

80 to 100 cm and surface samples were collected at a depth of 0 to 20 cm. Soils were air-dried, passed through a 2-mm sieve, and stored in closed containers at laboratory conditions before use. Soils were acidic and had variable-charge surfaces. Iron and aluminum oxides, kaolinite, and allophane were found as dominant minerals for all soils except for the Toronto soil in which smectite is dominant, thus Toronto soil has the smallest AEC. Clay-size quartz (<2 μ m) was found in DRC, K1, K2, K3, and Toronto soils; the amount of quartz in all other soils was negligible. Selected soil characteristics including pH, organic carbon content, CEC, and AEC are summarized in Table 1. Details with regard to soil classification, mineral identification, and characterization methods were previously reported (Hyun et al., 2003).

Chemicals

Prosulfuron was purchased from Chem Service (West Chester, PA) with reported purity of >98%. Prosulfuron has a molecular weight of 149.38, a pK_a of 3.76, and aqueous solubility of 30 mg L⁻¹ at pH = 5.1 and 3580 mg L⁻¹ at pH = 6.8 (Weed Science Society of America, 2002). The log K_{ow} value for the neutral species is 2.79 (extrapolated value from log K_{ow} values measured at pH = 5 and pH = 9) and for the anionic species is -0.76 measured at pH = 9 (Weed Science Society of America, 2002). Calcium chloride dihydrate (CaCl₂·2H₂O) was purchased from Fisher Scientific. Calcium bis(dihydrogenphosphate) monobasic and ammonium fluoride were purchased from Fluka (Buchs, Switzerland). Acetonitrile at greater than 99% purity was purchased from Mallinckrodt Baker (Phillipsburg, NJ).

Sorption Studies

Sorption was measured from pH-adjusted aqueous solutions consisting of 0.05, 5, or 500 mM CaCl₂ and 5 mM Ca(H₂PO₄)₂. Preweighed 35-mL glass tubes equipped with Teflon-lined screw caps were used. Sorbent to solution ratios (g mL⁻¹) ranged from 1:400 to 1:5 to achieve 20 to 80% sorption of the applied chemical after a 24-h contact time, but were fixed for a given isotherm. Prosulfuron solutions to be applied to soils were prepared in CaCl₂ and Ca(H₂PO₄)₂ solution by diluting acetonitrile solution containing a high concentration (1000 mg L⁻¹) of prosulfuron; final acetonitrile concentration was less than 0.5 vol. %. Isotherms consisted of five initial solute concentrations ranging from 1.19 to 9.54 μ M. Soil solutions were pH-adjusted using 0.1 M NaOH or 0.1 M HCl.

Table 1. Selected physical and chemical properties of soils.

Soil†	Subgroup	pH‡	Clay		AEC¶		CEC#	PZNC††	Major mineralogy‡‡
			%		cmol kg ⁻¹				
A1	Petroferric Hapludox	6.1	41	1.38	0.42	1.71	5.1	Gb > Go	
A2	Humic Rhodic Hapludox	5.2	77	1.17	0.53	3.32	3.0	Gb > He, K	
A3	Humic Rhodic Eutrudox	5.6	82	0.70	0.38	3.91	1.7	K > He	
DRC	Typic Hapludox	4.7	81	1.34	0.72	3.34	3.1	K > Gb, Go, He, Qz	
4R	-	5.3	59	2.04	0.25	8.07	<1	K >> C > Gb	
8R	-	5.7	47	2.33	0.20	10.4	<1	K >> C > Gb	
K1	Typic Dystrandept	5.2	27	8.97	0.77	16.7	1.9	K > A, Qz, C	
K2	Udic Eutrandept	5.0	39	4.45	0.41	21.8	<1	K > A, Qz, C	
K3	Typic Dystrandept	4.7	39	15.3	0.92	16.9	<1	K > A, Qz, C	
Toronto	Udolic Epiaqualfs	5.0	20	1.43	0.03	12.1	<1	S, Qz >> M > K	

† Soils included four highly weathered subsurface Oxisols (A1, A2, A3, and DRC) collected from Brazil, three subsurface Andisols (K1, K2, and K3) from South Korea, two weathered surface Ultisols (4R and 8R) from Costa Rica, and one moderately weathered surface Alfisol (Toronto) from Indiana.

‡ 1:10 (g mL⁻¹) H₂O.

§ Organic carbon.

¶ Anion exchange capacity at the pH value reported for soil-water slurries.

Cation exchange capacity at the pH value reported for soil-water slurries.

†† Point of zero net charge.

‡‡ C, chlorite; Gb, gibbsite; Go, goethite; He, hematite; K, kaolinite; M, mica; A, allophane; S, smectite. Greater than signs indicate mineral amount relative to other minerals identified; the absence of a sign between minerals indicates the relative amounts are approximately the same.

Soil and pH-adjusted electrolyte solution were rotated end-over-end (30 rpm) for 24 h at $23 \pm 2^\circ\text{C}$. All samples were performed in duplicate. The samples were centrifuged and supernatant aliquots were transferred to amber HPLC vials for analysis. The soils were extracted for 12 h by shaking with 10 mL 4:1 (v/v) acetonitrile and 0.25 M NH_4F solution. The prosulfuron concentration in supernatants and extracts of the soil were measured using a Shimadzu (Kyoto, Japan) high performance liquid chromatography (HPLC) system equipped with UV detector ($\lambda = 224 \text{ nm}$) and a Supelcosil ABZ-plus reverse-phase column (15-cm length \times 4.6-mm i.d., 5- μm particle size; Supelco, Bellefonte, PA). The mobile phase was 50:50 (v/v) acetonitrile and phosphate buffer (pH = 2.2) at a flow rate of 1 mL min^{-1} . Solute mass extracted was assumed to be the reversibly sorbed concentration.

Sorption isotherms were fit with linear ($C_s = K_d C_w$) and Freundlich ($C_s = K_f C_w^N$) sorption models where C_s ($\mu\text{mol kg}^{-1}$) and C_w ($\mu\text{mol L}^{-1}$) are equilibrium sorbed and solution concentrations, respectively, K_d is the linear sorption coefficient (L kg^{-1}), K_f is the Freundlich sorption coefficient ($\mu\text{mol}^{1-N} \text{ L}^N \text{ kg}^{-1}$), and N (unitless) is a measure of isotherm nonlinearity.

RESULTS AND DISCUSSION

Prosulfuron undergoes hydrolysis; therefore, sorption isotherms were generated by direct measurement of the solution- and sorbed-phase concentrations. Mass recovery from the sorbed and solution phases relative to the mass applied was pH-dependent with 30 to 50% recoveries at the most acidic pH (pH = 3.4) and 90 to 100% at neutral pH values. Recoveries versus pH followed similar trends observed for hydrolysis of prosulfuron in aqueous solutions (Bray et al., 1997). Metabolite peaks were observed in the chromatograms; however, inadequate chromatographic peak separation precluded quantification, and metabolite identification was not attempted.

Linear and Freundlich models were fit to the prosulfuron isotherms measured on model sorbents and variable-charge soils (Tables 2 and 3). The goodness of fit

(r^2) values for linear and Freundlich fits were greater than 0.95 in most cases with the exception of prosulfuron sorption by highly weathered subsurface Oxisols (A1) in 5 mM $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ($r^2 = 0.82$), where prosulfuron sorption was low ($K_d = 0.11 \text{ L kg}^{-1}$). The Freundlich K_f and linear sorption coefficient K_d values are within the 95% confidence intervals in most cases, suggesting that a linear estimation is adequate within the range of equilibrium aqueous concentrations obtained in this study (0.4–7.3 μM), in agreement with several sulfonyl-urea sorption studies (Borggaard and Streibig, 1989; Ukrainczyk and Ajwa, 1996; Werkheiser and Anderson, 1996).

Prosulfuron Sorption on Model Sorbents

Apart from prosulfuron sorption on humic acid (HA), in which hydrophobic interactions are most likely, the highest prosulfuron sorption was observed on QA-52, followed by α -alumina and amorphous silica, and sorption was negligible on CaSWy1. The trend in prosulfuron sorption across these sorbents can be explained by electrostatic interactions and pH-dependent charge distribution of both the sorbent surface and prosulfuron. Because of the high anion exchange capacity of QA-52 (103 cmol kg^{-1}) relative to prosulfuron spiked, prosulfuron sorption on QA-52 is primarily due to anion exchange between prosulfuron and chloride ions on the positively charged surface sites of the resin. The anion exchange of prosulfuron on QA-52 is proportional to the fraction of anionic species in the aqueous phase, thus sorption increases with increasing pH (Table 2). The AEC of QA-52 is >140 times larger than the moles of prosulfuron added and is not pH-dependent; therefore, sorption as a function of pH is attenuated by only prosulfuron speciation. On α -alumina, surface charge speciation dominated sorption such that sorption increased at the lower pH even though ionization of prosulfuron decreased.

Table 2. Coefficients from linear and Freundlich model fits to prosulfuron isotherms on model sorbents measured from 5 mM CaCl_2 solutions.

Sorbent†	PZNC‡	f_{oc} §	pH¶	f_a #	AEC††	CEC††	K_d	K_f	N
SiO_2	2.6	<0.000	3.5	0.36	0.19	0.53	1.65 (0.08)‡‡	1.75 (0.06)	0.89 (0.07)
			7.1	1.00	<0.001	1.26	ND§§	ND	ND
Al_2O_3	7.4	<0.000	3.8	0.53	7.43	0.41	4.20 (0.12)	4.43 (0.11)	0.84 (0.05)
			6.4	1.00	5.78	3.47	1.86 (0.12)	2.47 (0.28)	0.79 (0.09)
CaSWy1	NA	<0.000	3.6	0.38	–¶¶	76.4	ND	ND	ND
			8.0	1.00	–	–	ND	ND	ND
HA	2.5, 10.8	0.38	3.4	0.32	–	400 to approximately 900	148 (18)	180 (11)	0.72 (0.09)
			7.4	1.00	–	–	3.67 (0.37)	5.19 (1.38)	0.74 (0.24)
QA-52	NA	–	3.4	0.29	103	–	38.3 (0.9)	38.2 (1.1)	0.98 (0.04)
			4.7	0.91	–	–	61.1 (3.4)	62.1 (2.7)	0.99 (0.06)
			8.7	1.00	–	–	82.4 (4.4)	87.6 (3.1)	0.92 (0.05)

† SiO_2 , amorphous silica; Al_2O_3 , α -alumina; CaSWy1, a type of montmorillonite; HA, humic acid; QA-52, a type of anion exchange resin.

‡ Point of zero net charge. For silicate and alumina, PZNC values were measured in this study using the KCl method (Zelazny et al., 1996). For CaSWy1 and QA-52, PZNC is unlikely to be measurable because of fairly high and constant negative (or positive) charge. Reported values for HA are two estimated pK_a values (Tan and Giddens, 1972).

§ Organic carbon content.

¶ Average isotherm pH with a standard deviation of <0.1.

Fraction of prosulfuron anion.

†† Anion exchange capacity and cation exchange capacity of silicate and alumina were measured using the KCl method (Zelazny et al., 1996) in this study. The AEC of QA-52 is from the manufacturer. The CEC of HA and CaSWy1 are from Sposito (1989) and Van Olphen and Fripiat (1979), respectively.

‡‡ Values in the parentheses are the 95% confidence intervals.

§§ Not detectable. Measured sorbed prosulfuron mass was less than 2% of initially spiked mass or negative sorption.

¶¶ Negligible AEC or CEC.

Table 3. Coefficients from linear and Freundlich model fits to prosulfuron isotherms on model sorbents measured from 5 mM CaCl₂ and Ca(H₂PO₄)₂ solutions.

Soil†	pH	<i>f_a</i> ‡	OC§	AEC	CEC	Matrix#	<i>K_d</i>	<i>K_f</i>	<i>N</i>	<i>f_{hydrophilic}</i> ††
			%	— cmol kg ⁻¹ —			L kg ⁻¹	μmol ^{1-N} L ^N kg ⁻¹		
A1	5.8	0.99	1.38	0.54	1.46	Cl	0.62 (0.02)‡‡	0.67 (0.04)	0.93 (0.06)	0.82
						P	0.11 (0.01)	0.15 (0.05)	0.75 (0.22)	
A2	4.4	0.85	1.17	0.74	2.57	Cl	3.21 (0.18)	3.78 (0.13)	0.83 (0.05)	0.64
						P	1.16 (0.10)	1.78 (0.23)	0.92 (0.16)	
A3	5.0	0.94	0.70	0.93	7.08	Cl	0.71 (0.32)	0.98 (0.05)	0.77 (0.05)	0.44
						P	0.40 (0.19)	0.50 (0.08)	0.82 (0.15)	
DRC	4.2	0.73	1.34	0.96	2.76	Cl	7.19 (0.22)	8.61 (0.24)	0.83 (0.03)	0.66
						P	2.48 (0.17)	3.17 (0.39)	0.81 (0.12)	
4R	4.8	0.90	2.04	0.32	8.67	Cl	1.06 (0.06)	1.44 (0.04)	0.83 (0.02)	0.26
						P	0.79 (0.05)	0.79 (0.12)	0.99 (0.12)	
8R	4.8	0.92	2.33	0.30	7.20	Cl	2.49 (0.19)	3.17 (0.17)	0.81 (0.06)	0.23
						P	1.91 (0.14)	2.32 (0.16)	0.84 (0.08)	
K1	4.7	0.87	8.97	1.08	13.51	Cl	7.46 (0.82)	8.74 (0.29)	0.85 (0.04)	0.19
						P	6.05 (0.71)	7.31 (0.12)	0.82 (0.02)	
K2	4.2	0.69	4.45	0.58	17.97	Cl	7.36 (0.44)	8.53 (0.26)	0.82 (0.04)	-0.02
						P	7.50 (0.52)	8.86 (0.35)	0.79 (0.06)	
K3	4.3	0.78	15.3	1.08	14.80	Cl	6.51 (0.60)	7.19 (0.20)	0.89 (0.04)	0.12
						P	5.76 (0.58)	6.39 (0.13)	0.89 (0.03)	
Toronto	4.3	0.78	1.43	0.04	11.24	Cl	3.52 (0.06)	4.33 (0.20)	0.79 (0.06)	-0.05
						P	3.70 (0.05)	4.40 (0.13)	0.80 (0.04)	

† Soils included four highly weathered subsurface Oxisols (A1, A2, A3, and DRC) collected from Brazil, three subsurface Andisols (K1, K2, and K3) from South Korea, two weathered surface Ultisols (4R and 8R) from Costa Rica, and one moderately weathered surface Alfisol (Toronto) from Indiana.

‡ Fraction of prosulfuron existing as an anion calculated using a p*K_a* value of 3.76.

§ Organic carbon.

|| Anion exchange capacity and cation exchange capacity at the isotherm pH estimated from curve fits to measured exchange capacities as a function of pH (Hyun et al., 2003).

Cl and P represent 5 mM CaCl₂ and Ca(H₂PO₄)₂ solutions, respectively.

†† Fraction of phosphate-suppressed sorption calculated using Eq. [1].

‡‡ Values in parentheses are the 95% confidence intervals.

Prosulfuron exhibited no affinity for CaSWy1 in the pH range investigated (Table 2), which we attribute to repulsion between prosulfuron anions and the permanent negative charge on CaSWy1 mineral surface. Several studies have shown that weakly acidic pesticides, including phenoxyacetic acids and other sulfonylurea herbicides (chlorsulfuron and primisulfuron), are electrostatically repelled by the negatively charged clay particles when surface is in excess of negative charge (Borggaard and Streibig, 1988; Celis et al., 1999; Weber et al., 1965). Similar behavior was observed with amorphous silica at near-neutral pH where the surface is essentially completely negatively charged (pH \gg PZNC). At pH = 3.5, where a significant amount of AEC develops as the pH value approaches the PZNC (pH = 2.6; Table 2) and 36% of prosulfuron is still anionic (Table 2), significant prosulfuron was sorbed. Relative to AEC alone, prosulfuron sorption on amorphous silica at the acidic pH is much greater than observed on α -alumina. For example, prosulfuron sorption on silica per unit positive charge at pH = 3.5 (8.68 L cmol⁻¹) was much greater than observed on α -alumina at pH = 3.8 (0.57 L cmol⁻¹) and 6.4 (0.32 L cmol⁻¹). However, trends in anion sorption (*K_d*, L kg⁻¹) correlate well to the ratio of AEC to CEC at the isotherm pH (*r*² = 0.99, figure not shown). Correlation with only AEC is poor (*r*² = 0.53, figure not shown). The improved correlation when AEC is normalized to CEC exemplifies that negative charge (CEC) blocks the access of organic anion to positive charge site (AEC) on the soil surface. Sorption of several pesticides on silica has often been attributed to hydrogen bonding between the silanol (Si-OH) group and electron-drawing functional groups in the pesticides (Elder and Springer, 1940; Haque and Sexton, 1968; Ukrainczyk

and Ajwa, 1996); however, such mechanisms do not appear needed to explain prosulfuron sorption on these model sorbents.

For commercial HA, no anion exchange sites are present, thus sorption is primarily from hydrophobic interactions. Sorption as a function of pH was controlled by both speciation of prosulfuron and humic acid surface sites (e.g., carboxylic acid and phenolic functional groups), and differences in hydrophobicity of neutral and anionic prosulfuron. Assuming that the extent of prosulfuron sorption by HA is determined by hydrophobic sorption of neutral and ionized species (Lee et al., 1990), the log *K_{oc}* values of prosulfuron measured by sorption on commercial HA were 2.75 and 0.98 for neutral and ionized species, respectively. As pH increases, humic acid and prosulfuron will deprotonate, leading to a negatively charged sorbent surface and anionic prosulfuron, which results in decreasing sorption. Therefore, limited prosulfuron sorption at pH = 7.4 was observed relative to sorption at the acidic pH.

Prosulfuron Sorption on Variable-Charge Soils

Organic acid sorption to positively charged soil surface sites is blocked in the presence of specifically sorbed phosphate (Appelt et al., 1975; Ryden et al., 1987); therefore, the fraction of prosulfuron sorption suppressed in the 5 mM Ca(H₂PO₄)₂ relative to sorption in 5 mM CaCl₂ was assumed to represent hydrophilic sorption of prosulfuron. This assumption was hypothesized and proved reasonable in estimating the extent of anion exchange of acidic pesticide sorption on variably charged sorbents (Kavanagh et al., 1977; Madrid and Diaz-Barrientos, 1991; Hyun et al., 2003). The effect of

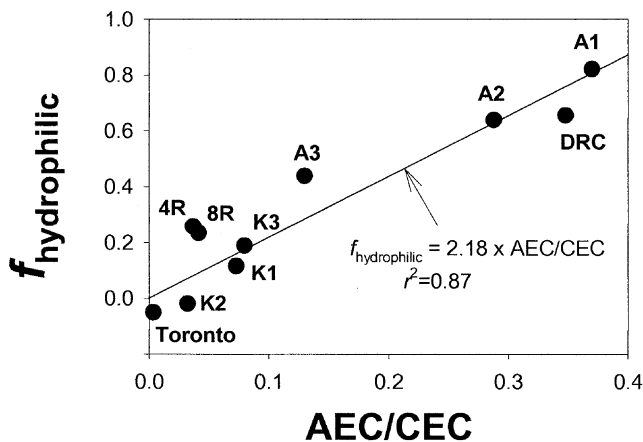


Fig. 1. Correlation between the fraction of hydrophilic prosulfuron sorption ($f_{\text{hydrophilic}}$) and the ratio of the absolute value of anion exchange capacity (AEC, cmol kg^{-1}) to cation exchange capacity (CEC, cmol kg^{-1}) at the pH of the prosulfuron isotherm study. The line is a linear regression fit set to intercept zero and r^2 is the associated goodness of fit. Soils include four highly weathered subsurface Oxisols (A1, A2, A3, and DRC) collected from Brazil, three subsurface Andisols (K1, K2, and K3) from South Korea, two weathered surface Ultisols (4R and 8R) from Costa Rica, and one moderately weathered surface Alfisol (Toronto) from Indiana.

dissolved phosphate on organic acid sorption to hydrophobic domains was found to be negligible (Nearpass, 1976), supporting dominant hydrophobic sorption in 5 mM $\text{Ca}(\text{H}_2\text{PO}_4)_2$ solution. The fraction of phosphate-suppressed sorption was assumed to be the fraction of prosulfuron sorption by hydrophilic domains ($f_{\text{hydrophilic}}$) and was calculated as follows:

$$f_{\text{hydrophilic}} = [K_d(\text{Cl}) - K_d(\text{P})]/K_d(\text{Cl}) \quad [1]$$

where $K_d(\text{Cl})$ and $K_d(\text{P})$ are the linear sorption coefficients of prosulfuron from 5 mM CaCl_2 and 5 mM $\text{Ca}(\text{H}_2\text{PO}_4)_2$, respectively.

The fraction of hydrophilic prosulfuron sorption ($f_{\text{hydrophilic}}$, unitless) ranges from negligible to 0.82 and correlates well to the ratio of soil AEC (cmol kg^{-1}) to CEC (cmol kg^{-1}) measured at the isotherm pH values ($r^2 = 0.87$; Fig. 1). Correlation of $f_{\text{hydrophilic}}$ to only AEC led to poor fits ($r^2 = 0.05$, figure not shown), similar to what was observed for prosulfuron on model sorbents and pentachlorophenolate sorption on variable-charge soil (Hyun et al., 2003). Normalizing AEC by CEC reasonably accounts for the repulsion by negatively charged sites on the soil surface. For example, Korean soils have AEC values similar or higher than Oxisols, but hydrophilic sorption ($f_{\text{hydrophilic}}$) was small to negligible. However, Korean soils have the highest CEC values resulting in small AEC to CEC ratios, which are consistent with the lesser hydrophilic sorption than observed. Clearly, the negative surface charge (CEC) attenuates the ability of organic anions to interact with the positively charged sites on the same surface. Note that since $f_{\text{hydrophilic}}$ is bounded between 0 and 1, the simple correlation illustrated in Fig. 1 is limited to $\text{AEC} \leq (\text{CEC}/2.18)$ or 0.46CEC . For all soils in this study except highly weathered subsurface Oxisols (A1), such conditions would not have been encountered in the pH range likely to occur naturally ($\text{pH} > 4$). The A1 soil has the highest PZNC (5.1) in which case a pH of approximately 5.5 would have met the limiting criteria.

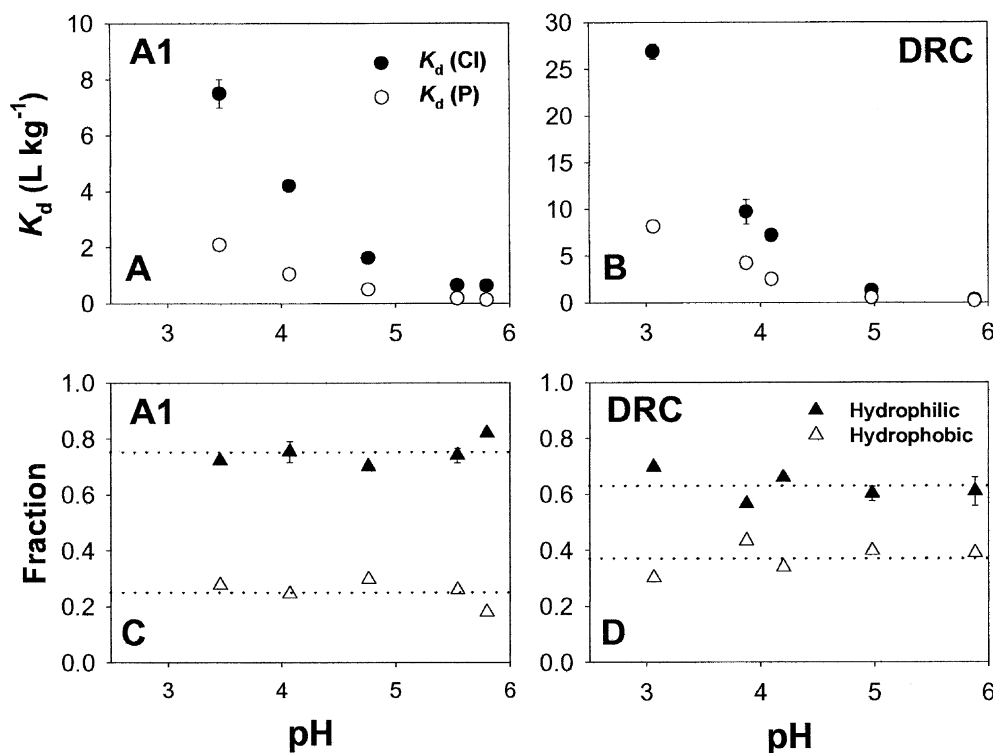


Fig. 2. pH dependence on the prosulfuron sorption coefficient (K_d , L kg^{-1}) measured from CaCl_2 and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ solutions (A and B), and the fraction of hydrophilic and hydrophobic prosulfuron sorption (C and D) for the highly weathered subsurface Oxisols A1 and DRC. The terms $K_d(\text{Cl})$ and $K_d(\text{P})$ noted in the legend refer to K_d values measured from 5 mM CaCl_2 and $\text{Ca}(\text{H}_2\text{PO}_4)_2$, respectively.

Prosulfuron Sorption as a Function of pH

The effect of pH on prosulfuron sorption (K_d , $L\ kg^{-1}$) from $CaCl_2$ and $Ca(H_2PO_4)_2$ was measured. The K_d values were estimated in duplicate for each pH value from a single aqueous equilibrium concentration (C_w) that was approximately mid-range of the C_w values observed in the whole isotherms for the same soil. Estimated K_d values measured from two solutions at a single prosulfuron concentration as a function of pH and the K_d determined from a multiconcentration isotherm at the natural soil pH are shown in Fig. 2A and 2B for highly weathered subsurface Oxisols (A1 and DRC). Differences in sorption between the two electrolytes decrease with increasing pH until no differences are observed. The pH at which there was no significant effect of electrolyte composition on sorption is proportional to the soil PZNC; the higher the soil PZNC, the higher the pH value before there is no observable electrolyte effect on sorption. Similar trends in sorption with electrolyte composition, pH, and PZNC were observed for all soils.

The fractions of prosulfuron sorption attributed to hydrophobic and hydrophilic (primarily anion exchange) as a function of pH are shown in Fig. 2C and 2D for highly weathered subsurface Oxisols (A1 and DRC), respectively. With increasing pH, AEC decreases and CEC increases, thus reducing anion exchange, and likewise, the neutral prosulfuron fraction decreases, reducing hydrophobic sorption. The net effect for both soils is an approximately constant contribution from each mechanism as a function pH, suggesting that the relative contribution from each mechanism per unit pH change is similar. All soils exemplified similar trends with the hydrophilic fraction of sorption across all pH values being 0.04 to 0.1 pH units of the values estimated at the natural soil pH as reported in Table 3.

In previous studies with pentachlorophenol (Lee et al., 1990) and prosulfuron (Hultgren, 2000), sorption as a function of pH was reasonably described by assuming that (i) there was only pH-dependent speciation of the solute and (ii) differences in the magnitude of sorption at low and high pH was due to differences in the hydrophobicity of the neutral and anionic solute species, thereby, allowing the use of OC-normalized sorption coefficients ($\log K_{oc}$). With the assumption of only hydrophobic sorption, the $\log K_{oc}$ values for the neutral and anionic species were estimated from fits to the $\log K_{oc}$ -pH curve (Lee et al., 1990). Specific hydrophilic sorption (i.e., ligand exchange) or pH-dependent speciation of soil functional groups were not considered. The $\log K_{oc}$ values for prosulfuron estimated from the sorption data from 5 mM $CaCl_2$ in this study as well as those reported by Hultgren (2000) for 18 U.S. soils in 10 mM $CaCl_2$ are plotted as a function of pH in Fig. 3. The $\log K_{oc}$ values reported by Hultgren (2000) were calculated using sorbed concentrations that were estimated by difference (any prosulfuron not detected in the aqueous phase at equilibrium relative to the applied concentration was considered sorbed) with the exception of the lowest pH data (pH = approximately 4). Therefore, loss of parent compound by hydrolysis or biological

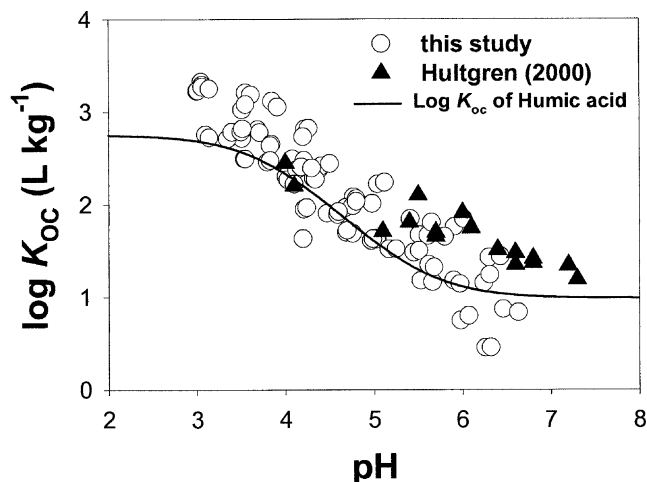


Fig. 3. $\log K_{oc}$ ($L\ kg^{-1}$ organic carbon [OC]) of prosulfuron as a function of pH collected from this study (open circles) and for 18 soils from Hultgren (2000; closed triangles). The solid line is $\log K_{oc}$ as a function of pH estimated by weighted combination of two $\log K_{oc}$ values of neutral and ionized species for commercial humic acid measured in this study.

degradation was attributed to sorption in all but the most acidic pH systems, thus over estimating $\log K_{oc}$ values. Also shown in Fig. 3 is a line for prosulfuron sorption by commercial humic acid as a function of pH that was predicted using the $\log K_{oc}$ values estimated for the neutral and ionized species from sorption data obtained in this study. For humic acid, sorption is primarily through hydrophobic-type interactions. Typically, $\log K_{oc}$ values of several nonpolar chemicals reported for commercial humic acid are at least 0.5 log units greater than $\log K_{oc}$ values estimated for natural soils, which has been attributed to the greater hydrophobicity of commercial humic acid relative to soil organic matter (Schwarzenbach et al., 2003, p. 302 and 319). Clearly, most of the sorption data from soils are above the line for humic acid, indicating sorption by more than just hydrophobic interactions. Even so, Fig. 3 clearly exemplifies the pH-dependence of prosulfuron sorption normalized to OC regardless of whether the primary sorption mechanism is hydrophilic or hydrophobic. The latter may coincidentally result from the fact that (i) with increasing OC content CEC increases, thus effective AEC is reduced, and (ii) with increasing pH, the relative change in hydrophobic and hydrophilic sorption mechanisms is relatively constant.

Effect of Increasing Inorganic Ion Concentration on Prosulfuron Sorption

To further assess the role of hydrophilic and hydrophobic interactions for prosulfuron, sorption by highly weathered subsurface Oxisols (DRC) and Toronto series soil was measured from solutions varying in $CaCl_2$ concentration. Increasing $CaCl_2$ concentration (0.05–500 mM) may induce several competing effects in an acidic pesticide–soil system (Escher and Schwarzenbach, 1996; Schwarzenbach et al., 2003, p. 302 and 319) including (i) increased competition for sorption sites by the background electrolyte anion chloride, (ii) decreased

anionic pesticide activity and increased protonated pesticide activity in aqueous solution, and (iii) increased ion pairing and subsequent sorption of ion pairs, if any. The first two effects will result in decreasing the anionic pesticide sorption by hydrophilic domains while the second and third effects will result in an increase in hydrophobic sorption.

The DRC and Toronto soils were selected because their natural soil pH values and organic carbon content are similar while exhibiting very different sorption behavior; DRC exhibited the highest contribution from hydrophilic sorption and Toronto showed no measurable contribution. For DRC, where appreciable amounts of anion exchange of prosulfuron were estimated, a fivefold decrease in sorption going from 0.0015 to 1.5 M CaCl₂ was indicative of competition for sorption sites by the chloride ion consistent with an anion exchange process. For the Toronto soil, changes in prosulfuron sorption with increasing ionic strength were not statistically significant ($3.54 \pm 0.02 \text{ L kg}^{-1}$), supporting the absence of anion exchange. Both the second and third effects above, which would result in an increase in sorption with increasing ionic strength, were not apparent.

CONCLUSIONS

Hydrophilic sorption controlled by anion exchange processes is important for estimating prosulfuron sorption by variable-charge soils. Consistent with the previous studies (Hyun et al., 2003), the interaction of organic anions with anion exchange sites was attenuated by excess negative charge on the sorbent surface. Both anion exchange and hydrophobic sorption of prosulfuron exhibited decreasing sorption with increasing pH. Comparison between OC-normalized sorption (K_{oc}) versus pH for humic acid and variable-charge soils show similar trends with sorption decreasing with increasing pH. However, K_{oc} values in the lower pH range where anion exchange has the greatest contribution to sorption by variable-charge soils was almost one log unit greater than that estimated from humic acid, clearly exemplifying the effect of anion exchange. Similarity in K_{oc} -pH curves for humic acid and variable-charge soils may be a consequence of the following: (i) CEC increases with increasing OC content, thus effective AEC is reduced, and (ii) the relative contribution in hydrophobic and hydrophilic sorption mechanisms is relatively constant over the pH range investigated. Often soil amendments such as limestone, gypsum, and calcium phosphate are added to acidic soils to increase pH and enhance their fertility. Given that both hydrophilic and hydrophobic sorption as well as hydrolysis of prosulfuron decreases with increasing pH, addition of such amendments may result in off-site leaching of recently applied acidic pesticides. Likewise, addition of salts through such amendments will also decrease sorption from competition of inorganic anions for anion exchange sites, which may further enhance the likelihood of mobility.

REFERENCES

- Appelt, H., N.T. Coleman, and P.F. Pratt. 1975. Interactions between organic compounds, minerals and ions in volcanic-ash-derived soils: II. Effects of organic compounds on the adsorption of phosphate. *Soil Sci. Soc. Am. Proc.* 39:628–630.
- Beckie, H.J., and R.B. McKercher. 1990. Mobility of two sulfonylurea herbicides in soil. *J. Agric. Food Chem.* 38:310–315.
- Borggaard, O.K., and J.C. Streibig. 1988. Chlorsulfuron adsorption by humic acid, iron oxide, and montmorillonite. *Weed Sci.* 36:530–534.
- Borggaard, O.K., and J.C. Streibig. 1989. Chlorsulfuron adsorption by selected soil sample. *Acta Agric. Scand.* 39:351–360.
- Bray, L.D., N.E. Heard, M.C. Overman, J.D. Vargo, D.L. King, L.J. Lawrence, and A.W. Phelps. 1997. Hydrolysis of prosulfuron at pH 5: Evidence for a resonance-stabilized triazine cleavage product. *Pestic. Sci.* 51:56–64.
- Cambon, J.P., S.Q. Zheng, and J. Bastide. 1992. Chemical or microbial degradation of sulfonylurea herbicides in soil. I. The case of sulfometuron methyl. *Weed Res.* 32:1–7.
- Celis, R., M.C. Hermosin, L. Cox, and J. Cornejo. 1999. Sorption of 2,4-dichlorophenoxyacetic acid by model particles simulating naturally occurring soil colloids. *Environ. Sci. Technol.* 33:1200–1206.
- Dinelli, G., A. Vicari, A. Bonetti, and P. Catizone. 1997. Hydrolytic dissipation of four sulfonylurea herbicides. *J. Agric. Food Chem.* 45:1940–1945.
- Elder, A.L., and R.A. Springer. 1940. Application of the hydrogen-bridge theory to sorption from solution by silica gel. *J. Phys. Chem.* 44:943–949.
- Escher, B.L., and R.P. Schwarzenbach. 1996. Partitioning of substituted phenols in liposome-water, biomembrane-water, and octanol-water systems. *Environ. Sci. Technol.* 30:260–270.
- Fletcher, J.S., T.G. Pfleeger, and H.C. Ratsch. 1993. Potential environmental risks associated with the new sulfonylurea herbicides. *Environ. Sci. Technol.* 27:2250–2252.
- Goyno, K.W., A.R. Zimmerman, B.L. Newalkar, S. Komarneni, S.L. Brantley, and J. Chorover. 2002. Surface charge of variable porosity Al₂O₃(s) and SiO₂(s) adsorbents. *J. Porous Mater.* 9:243–256.
- Haque, R., and R. Sexton. 1968. Kinetic and equilibrium study of the adsorption of 2,4-dichlorophenoxyacetic acid on some surface. *J. Colloid Interface Sci.* 27:818–827.
- Hultgren, R.P. 2000. Sorption and degradation of prosulfuron. M.S. thesis. Univ. of Illinois, Urbana-Champaign.
- Hultgren, R.P., R.J.M. Hudson, and G.K. Sims. 2002. Effects of soil pH and soil water content on prosulfuron dissipation. *J. Agric. Food Chem.* 50:3236–3243.
- Hyun, S., L.S. Lee, and P.S.C. Rao. 2003. Significance of anion exchange in pentachlorophenol sorption by variable-charge soils. *J. Environ. Qual.* 32:966–976.
- Joshi, M.M., H.M. Brown, and J.A. Romesser. 1985. Degradation of chlorsulfuron by soil microorganisms. *Weed Sci.* 33:564–568.
- Kavanagh, B.V., A.M. Posner, and J.P. Quirk. 1977. The adsorption of phenoxyacetic acid herbicides on goethite. *J. Colloid Interface Sci.* 61:545–553.
- Kulowski, K., E.L. Zirbes, B.M. Thede, and J.P.N. Rosazza. 1997. Microbial transformations of prosulfuron. *J. Agric. Food Chem.* 45:1479–1485.
- Lee, L.S., P.S.C. Rao, P. Nkedi-Kizza, and J.J. Delfino. 1990. Influence of solvent and sorbent characteristics on distribution of pentachlorophenol in octanol-water and soil-water systems. *Environ. Sci. Technol.* 24:654–661.
- Madrid, L., and E. Diaz-Barrientos. 1991. Effect of phosphate on the adsorption of 2,4-D on lepidocrocite. *Aust. J. Soil Res.* 29:15–23.
- Menniti, C., J.-P. Cambon, and J. Bastide. 2003. Soil transformation of prosulfuron. *J. Agric. Food Chem.* 51:3525–3527.
- Mersie, W., and C.L. Foy. 1986. Adsorption, desorption, and mobility of chlorsulfuron in soils. *J. Agric. Food Chem.* 34:89–92.
- Nearpass, D.C. 1976. Adsorption of picloram by humic acids and humin. *Soil Sci.* 121:272–277.
- Pantani, O., L. Calamai, and P. Fusi. 1994. Influence of clay minerals on adsorption and degradation of a sulfonylurea herbicide (cinosulfuron). *Appl. Clay Sci.* 8:373–387.
- Ryden, J.C., J.K. Syers, and R.W. Tillman. 1987. Inorganic anion

- sorption and interactions with phosphate sorption by hydrous ferric oxide gel. *J. Soil Sci.* 38:211–217.
- Sarmah, A.K., and J. Sabadie. 2002. Hydrolysis of sulfonylurea herbicides in soils and aqueous solutions: A review. *J. Agric. Food Chem.* 50:6253–6265.
- Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden. 2003. *Environmental organic chemistry*. 2nd ed. John Wiley & Sons, New York.
- Shea, P. 1986. Chlorsulfuron dissociation and adsorption on selected adsorbents and soils. *Weed Sci.* 34:474–478.
- Sposito, G. 1989. *The chemistry of soils*. Oxford Univ. Press, New York.
- Tan, K.H., and J.E. Giddens. 1972. Molecular weights and spectral characteristics of humic and fulvic acids. *Geoderma* 8:221–229.
- Ukrainczyk, L., and H.A. Ajwa. 1996. Primisulfuron sorption on minerals and soils. *Soil Sci. Soc. Am. J.* 60:460–467.
- Van Olphen, H., and J.J. Fripiat. 1979. *Data handbook for clay materials and other non-metallic minerals*. Pergamon Press, Oxford.
- Walker, A., E.G. Cotterill, and S.J. Welch. 1989. Adsorption and degradation of chlorsulfuron and metsulfuron-methyl in soils from different depths. *Weed Res.* 29:281–287.
- Weber, J.B., P.W. Perry, and R.P. Upchurch. 1965. The influence of temperature and time on the adsorption of paraquat, diquat, 2,4-D and prometon by clays, charcoal, and an anion-exchange resin. *Soil Sci. Soc. Am. Proc.* 29:678–688.
- Weed Science Society of America. 2002. *Herbicide handbook*. 8th ed. Weed Sci. Soc. Am., Champaign, IL.
- Werkheiser, W.O., and S.J. Anderson. 1996. Effect of soil properties and surfactant on primisulfuron sorption. *J. Environ. Qual.* 25:809–814.
- Yopps, J.A., and D.W. Fuerstenau. 1964. The zero point of charge alpha-alumina. *J. Colloid Sci.* 19:61–71.
- Zelazny, L.W., L. He, and A. Vanwormhoudt. 1996. Charge analysis of soils and anion exchange. p. 1231–1253. *In* D.L. Sparks (ed.) *Methods of soil analysis*. Part 3. SSSA Book Ser. 5. SSSA, Madison, WI.