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Evaluation of Sorption Coefficients for Pyroxasulfone, *s*-Metolachlor, and Dimethenamid-*p*

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ABSTRACT: Sorption coefficients were evaluated for pyroxasulfone, *s*-metolachlor, and dimethenamid-*p* across 25 soil types with different chemical and physical properties to better understand how soil properties influence the binding of pyroxasulfone in different soils. Sorption coefficients were determined using a batch equilibrium method to evaluate relative differences in binding among the three herbicides. Based on water solubility values, we would have expected the relative order of binding to be dimethenamid-*p* (1450 mg L^{-1} at 20°C), *s*-metolachlor (530 mg L^{-1} at 20°C), and pyroxasulfone (3.49 mg L^{-1} at 20°C) in order of increasing binding. However, when sorption coefficients were calculated, we observed the order of pyroxasulfone = dimethenamid-*p* < *s*-metolachlor in the order of increasing binding. The average K_d (sorption coefficient) values were 1.7, 2.3, and 4.0 L kg^{-1} for pyroxasulfone, dimethenamid-*p*, and *s*-metolachlor, respectively. Although dimethenamid-*p* has water solubility values that are over 400 times greater than pyroxasulfone, there was no statistical difference in binding between pyroxasulfone and dimethenamid-*p*. *s*-Metolachlor binding was statistically greater than both pyroxasulfone and dimethenamid-*p*. Across all soil chemical and physical properties, sorption coefficients for all three herbicides were highly and statistically correlated to soil organic matter. Sand and silt were also statistically correlated to binding, although these correlations could be explained by the high correlation of organic matter to these properties. Evaluation of sorption coefficients indicates that pyroxasulfone is most prevalent in the soil solution where herbicides are available for plant uptake. Reduced soil binding and greater activity at the target site could contribute to comparable weed control efficacies of pyroxasulfone even when applied at lower use rates compared to either *s*-metolachlor or dimethenamid-*p*.

KEYWORDS: pyroxasulfone, sorption, metolachlor, dimenthenamid

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Introduction

Chloroacetamide herbicides for pre-emergence weed control in various crops were first introduced in the early 1950s and 1960s. Although some of the first compounds were eventually replaced, the addition of safeners has extended the use of chloroacetamide herbicides for broadening the weed control spectrum when used in tank mixes.[1] Acetanilide-derived herbicides are used for pre-emergence weed control in corn and soybean, as well as sorghum (*Sorghum bicolor*), sunflower (*Helianthus annuus*), peanut (*Arachis hypogaea*), and cotton (*Gossypium* spp.).[2]

Chloroacetamide herbicides are often used in tank-mixes with other herbicides to provide broad-spectrum weed control. These herbicides play a vital role in managing herbicide-resistant weeds, including those resistant to glyphosate, but their limited activity on many broadleaf weeds has increased the need for additional herbicide chemistries to achieve effective weed control. Evaluations of new herbicide compounds are crucial for the development of new types of chemistry for weed control and for incorporation of these compounds into cropping systems to give farmers more diverse tools to manage weeds that are inherently difficult to control.

Pyroxasulfone is a new, pyrazole-based herbicide with the same mechanism of action as chloroacetamides, eg, the inhibition of very long chain fatty acid biosynthesis.[3] This compound is used pre-emergent to control a broad spectrum of grasses and small-seeded broadleaves and is selective in corn, soybean, wheat, and sunflower.[4] The advantage of pyroxasulfone over the chloroacetamide herbicides is its low use rate and activity on important broadleaf weeds such as *Amaranthus* spp.[5] Pyroxasulfone recently received an Environmental Protection Agency (EPA) federal registration to be used in combination with flumioxazin in corn in the United States (Valent U.S.A. press release, 2011).

Herbicide sorption to soil influences a compound's environmental fate, persistence in the soil, and biological activity.[6] It is important to examine the affinity of pyroxasulfone to soil to provide insight into its interaction with soil when applied under field conditions. Soil texture and chemical properties influence herbicide binding and subsequent weed control. Understanding the influences of these properties on the binding of pyroxasulfone will help us predict the behavior of the compound in different soils. Pyroxasulfone has been shown to provide comparable weed control to chloroacetamide herbicides when applied at much lower use rates,[7] and investigating soil adsorption rates could provide insight into this difference in weed control efficacy in terms of amounts of available herbicide for plant uptake.

There have been numerous studies on how chloroacetamide herbicides bind to soil components. For example, soil organic matter is the predominant adsorbent for *s*-metolachlor.[6,8] This type of information is limited for pyroxasulfone, so we cannot compare soil interactions to commonly used chloroacetamide herbicides. Measuring the soil-sorption coefficients for pyroxasulfone and comparing these values to commonly used chloroacetamide herbicides will give us a predictor of how this compound will act in the field and how it can be incorporated into current agricultural practices.

The objectives of this study were to (a) compare the relative soil binding between pyroxasulfone, *s*-metolachlor, and dimethenamid-*p* across 25 different soil types and (b) evaluate the influence of different soil texture and chemical properties on soil binding of these three herbicides.

Materials and Methods

Herbicide soil adsorption. A mixed herbicide stock solution was prepared by combining 1 mg mL^{-1} of pyroxasulfone, *s*-metolachlor, and dimethenamid-*p* together in a 0.02 M $CaCl_2$ solution. Given that herbicide adsorption is a competitive process, pilot studies were conducted to confirm that adsorption rates at 1 mg mL^{-1} were similar for combined herbicide solutions compared to individually applied herbicides. Batch equilibrium studies were conducted by combining 10 g of dry soil with 10 mL of herbicide stock solution in capped, 50-mL glass centrifuge tubes, which were shaken horizontally for 24 hours on a table shaker. Control herbicide solutions without soil were also included and used for initial total herbicide concentrations in order to account for herbicide binding to glassware. After shaking, the samples were centrifuged at 1000 rcf (relative centrifugal force) for 10 minutes to separate the soil and herbicide solution. Three milliliters of the supernatant was combined with 3 mL of toluene and shaken for two hours on a horizontal shaker. After being centrifuged at 1000 rcf for 10 minutes, 2 mL of the toluene supernatant was transferred to a volumetric flask and spiked with 500 ng L^{-1} butylate as an internal standard and then injected in a gas chromatography/mass spectrometry (GC/MS) column to quantify herbicide concentrations in the solution. The herbicide concentrations in the toluene phase were analyzed using a gas chromatograph equipped with a mass spectrometer (Shimadzu GC-17A and GCMS QO 5050A, Shimadzu Scientific Instruments, Inc., Columbia, MD, USA), which monitored the masses for butylate (*m*/*z* 146), *s*-metolachlor (*m*/*z* 162.15), dimethenamid-*p* (*m*/*z* 229.10), and pyroxasulfone (*m*/*z* 179.10). An RTX-5 30-m × 0.25-mm column (Restek, Bellefonte, PA) was used with a flow of helium at 1 mL min^{-1}.

Herbicide concentrations in the liquid solution were subtracted from initial total concentrations without soil to calculate the amount of herbicide bound to the soil. Ratios were then calculated by dividing the concentration of herbicide bound to the soil by the concentration in the soil solution as mathematically represented by equation (1).

$$K_d = \frac{\text{Herbicide sorbed to soil } (\mu\text{g g}^{-1})}{\text{Herbicide in solution } (\mu\text{g mL}^{-1})} \tag{1}$$

K_{oc} for each herbicide was calculated as

$$K_{oc} = (K_d/f_{oc}) \times 100 \tag{2}$$

where f_{oc} is the soil organic C mass-fraction 100 g soil^{-1} that was measured for each soil f_{oc} was calculated as

$$f_{oc} = \text{som}/1.72 \tag{3}$$

where som is the soil organic matter and 1.72 is a conversion factor to estimate the fraction of organic carbon from the amount of soil organic matter.

Soil analysis. Soils were air dried and passed through a 2.0-mm screen. Two replicates of each soil were sent to AgSource/Harris Laboratories (Lincoln, NE, USA) and were analyzed for texture, pH, cation exchange capacity (CEC), and organic matter. Soil samples and their replicates were randomized and blindly labeled to ensure the objectivity, quality, and precision of analyses. Soil series information was not available for the collected soils used in evaluating herbicide sorption coefficients; therefore, conclusions about relative binding are restricted to the physical and chemical properties of the soils used.

Statistical analysis. Pearson correlations were calculated for sorption coefficients (K_d and K_{oc}) versus all soil textual and chemical properties with a significance level of $P < 0.05$ using the Multivariate function in JMP Pro version 10. Fisher's least significant difference (LSD) was calculated for the three herbicides using the statistical program SAS version 9.2.

Results

Herbicide sorption. Soil textural and chemical properties for all soils are listed in Table 1. The K_d and K_{oc} values for all three herbicides in different soils are displayed in Table 2. The greatest amount of herbicide adsorption for all three compounds occurred in the Dodge County, Wisconsin, silt loam soil. For *s*-metolachlor and dimethenamid-*p*, the lowest adsorption occurred in the Pasco, Washington, sand soil. For pyroxasulfone, the lowest amount of adsorption occurred in the 3-River Montana sandy clay loam soil. Sorption coefficients ranged from 0.76 to 16.67 L kg^{-1} for *s*-metolachlor, 0.32 to 9.57 L kg^{-1} for dimethenamid-*p*, and 0.49 to 5.91 L kg^{-1} for pyroxasulfone. When combined across all soil types, the mean and median K_d values were 4.0 and 2.8 L kg^{-1} for *s*-metolachlor, 2.3 and 1.7 L kg^{-1} for dimethenamid-*p*, and 1.7 and 1.5 L kg^{-1} for pyroxasulfone, respectively. Pearson correlations were calculated comparing K_d values to soil textural and chemical properties, which are displayed in Table 3.

When comparing the K_d values for all three herbicides, we observed a significant relationship with organic matter, silt, and sand at $r^2 = 0.89$, 0.63, and −0.52 for *s*-metolachlor; $r^2 = 0.92$, 0.65, −0.55 for dimethenamid-*p*; and $r^2 = 0.94$, 0.67, −0.66 for pyroxasulfone (Table 3). Soil pH, cation exchange capacity, and clay content were not significantly correlated to K_d for all three herbicides (Table 3). Correlations between organic matter, sand, and silt content resulted in significant linear relationships of −0.676 and 0.688, respectively (Table 4). High correlations among soil properties across all soils resulted in correlations between these soil properties and herbicide binding. Given that organic matter was highly correlated to herbicide binding (>0.89 for all herbicides), and also highly correlated to sand and silt content, this would explain the significant correlation with both sand and silt content and herbicide binding.

Fisher's LSD for all three herbicides was run across all soil types. Fisher's LSD = 0.6179, which resulted in statistical differences between *s*-metolachlor and both pyroxasulfone and dimethenamid-*p*, but there was no statistical difference between binding for pyroxasulfone and dimethenamid-*p* (Table 5). K_{oc} (organic carbon–water partitioning coefficient) is the distribution coefficient (K_d) normalized to total organic carbon content and is calculated from equation (2). K_{oc} values were calculated for all three herbicides across all soils. The average K_{oc} values ± standard error for *s*-metolachlor was 273 ± 23 L kg^{-1}, dimethenamid-*p* 151 ± 10 L kg^{-1}, and pyroxasulfone 117 ± 7 L kg^{-1}.

Table 1. Soil physical and chemical properties for the 25 soils that were evaluated in order of increasing organic matter.

	PH	OM %	CEC	% SAND	% SILT	% CLAY	TEXTURE
Pasco, WA	7.40	0.80	7.9	88.0	11.2	0.8	Sand
3 River, MT	6.40	1.10	4.8	62.0	37.2	0.8	Sandy Loam
LIRF, CO	8.00	1.10	19.8	70.0	19.2	10.8	Sandy Loam
Yuma, CO	8.00	1.10	20.3	62.0	31.2	6.8	Sandy Loam
FL	6.90	1.30	4.3	84.0	15.2	0.8	Loamy Sand
Ephrata, WA	6.35	1.35	10.9	82.2	16.6	1.2	Loamy Sand
Gilcrest, CO	7.50	1.50	10.2	84.0	15.2	0.8	Loamy Sand
NC	4.90	1.50	3.8	90.0	9.2	0.8	Sand
Holtville, CA	7.90	1.80	36.6	30.0	31.2	38.8	Clay Loam
Ardec, CO	8.20	1.90	23.6	55.2	17.6	27.2	Sandy Clay Loam
Mt King, MT	7.80	2.00	26.8	34.0	33.2	32.8	Clay Loam
IN	5.80	2.10	7.4	72.8	22.0	5.2	Sandy Loam
Cutbank, MT	7.85	2.15	18.3	52.2	28.6	19.2	Sandy Loam
Hort Farm, CO	8.00	2.20	32.0	34.0	25.2	40.8	Clay
Moscow, ID	6.50	2.25	14.4	24.2	59.6	16.2	Silt Loam
Pendelton, OR	5.80	2.25	11.4	27.2	65.6	7.2	Silt Loam
Bozeman, MT	7.20	2.30	22.0	27.8	51.0	21.2	Silty Loam
Mt Jossette, MT	7.90	2.60	27.7	48.0	23.2	28.8	Sandy Clay Loam
Chesterfield, MO	5.20	3.05	12.5	24.2	56.6	19.2	Silt Loam
Huntley, MT	7.85	3.20	30.2	10.2	39.6	50.2	Clay
Columbia County, WI	6.70	3.45	12.4	34.8	58.0	7.2	Silt Loam
Columbia County, WI	6.60	3.65	12.5	38.8	57.0	4.2	Silt Loam
Green Lake County, WI	7.10	3.85	13.8	17.8	75.0	7.2	Silt Loam
Saskatoon, CA	6.75	4.70	27.9	31.2	37.6	31.2	Clay Loam
Dodge County, WI	5.55	6.25	18.9	21.8	69.0	9.2	Silt Loam

Table 2. Sorption coefficients (K_d and K_{oc}) for *s*-metolachlor, dimethenamid-*p*, and pyroxasulfone in order of increasing organic matter.

	TEXTURE	OM %	*s*-METOLACHLOR				DIMETHENAMID-*p*				PYROXASULFONE			
			K_d	SE	K_{oc}	SE	K_d	SE	K_{oc}	SE	K_d	SE	K_{oc}	SE
			(L/kg)											
Pasco, WA	Sand	0.80	0.76	0.25	163	54	0.32	0.02	69	4	0.53	0.09	114	19
3 River, MT	Sandy Loam	1.10	1.64	0.18	256	28	0.82	0.07	128	11	0.49	0.05	77	8
LIRF, CO	Sandy Loam	1.10	1.37	0.08	214	13	0.71	0.01	111	2	0.55	0.06	86	9
Yuma, CO	Sandy Loam	1.10	1.40	1.29	219	202	0.72	0.61	113	95	0.64	0.16	100	25
FL	Loamy Sand	1.30	2.65	0.25	351	33	1.42	0.04	188	5	0.68	0.16	90	21
Ephrata, WA	Loamy Sand	1.35	1.26	0.09	161	11	0.64	0.06	82	8	0.54	0.03	69	4
Gilcrest, CO	Loamy Sand	1.50	2.37	0.08	272	9	1.06	0.05	122	6	0.62	0.02	71	2
NC	Sand	1.50	2.60	0.04	298	5	1.32	0.03	151	3	0.83	0.03	95	3
Holtville, CA	Clay Loam	1.80	5.01	0.12	479	11	2.84	0.25	271	24	1.98	0.02	189	2
Ardec, CO	Sandy Clay Loam	1.90	2.48	0.08	225	7	1.48	0.05	134	5	1.09	0.03	99	3
Mt King, MT	Clay Loam	2.00	2.30	0.19	198	16	1.32	0.03	114	3	1.40	0.08	120	7
IN	Sandy Loam	2.10	5.00	0.03	410	2	2.50	0.01	205	1	1.72	0.04	141	3
Cutbank, MT	Sandy Loam	2.15	3.77	0.11	302	9	1.94	0.04	155	3	1.90	0.04	152	3
Hort Farm, CO	Clay	2.20	2.25	0.12	176	9	1.38	0.05	108	4	0.84	0.12	66	9
Moscow, ID	Silt Loam	2.25	3.89	0.12	297	9	2.26	0.03	173	2	1.53	0.03	117	2
Pendelton, OR	Silt Loam	2.25	2.72	0.08	208	6	1.42	0.04	109	3	1.46	0.02	112	2
Bozeman, MT	Silty Loam	2.30	3.93	0.04	294	3	1.94	0.05	145	4	1.89	0.01	141	1
Mt Jossette, MT	Sandy Clay Loam	2.60	2.83	0.05	187	3	1.71	0.06	113	4	1.92	0.03	127	2
Chesterfield, MO	Silt Loam	3.05	7.32	0.05	413	3	3.97	0.23	224	13	3.28	0.05	185	3
Huntley, MT	Clay	3.20	3.19	1.37	171	74	1.98	0.15	106	8	2.20	0.39	118	21
Columbia County, WI	Silt Loam	3.45	4.58	0.25	228	12	3.89	0.08	194	4	2.16	0.09	108	4
Columbia County, WI	Silt Loam	3.65	4.85	0.03	229	1	2.72	0.03	128	1	1.97	0.04	93	2
Green Lake County, WI	Silt Loam	3.85	8.24	0.09	368	4	4.60	0.19	206	8	3.26	0.04	146	2
Saskatoon, CA	Clay Loam	4.70	7.13	0.32	261	12	4.43	0.77	162	28	3.72	0.11	136	4
Dodge County, WI	Silt Loam	6.25	16.67	1.17	459	32	9.57	0.01	263	0	5.91	0.38	163	10

Table 3. Pearson correlations were evaluated for *s*-metolachlor, dimethenamid-*p*, and pyroxasulfone K_d and K_{oc} values versus soil chemical and physical properties.

K_d CORRELATION	*s*-METOLACHLOR	DIMETHENAMID-*p*	PYROXASULFONE
OM	0.886*	0.917*	0.943*
pH	−0.418	−0.390	−0.331
CEC	0.096	0.126	0.247
Sand	−0.519*	−0.552*	−0.660*
Silt	0.628*	0.647*	0.669*
Clay	0.035	0.064	0.219
K_{oc} CORRELATION	***s*-METOLACHLOR**	**DIMETHENAMID-*p***	**PYROXASULFONE**
OM	0.346*	0.512	0.470*
pH	−0.404	−0.362*	−0.163
CEC	−0.081	0.047	0.306
Sand	−0.189	−0.366	−0.534*
Silt	0.303	0.432*	0.434*
Clay	−0.087	0.040	0.322

Note: *Significance at $\alpha = 0.05$.

Table 4. Pearson correlations between soil textural and chemical properties.

	PH	OM	CEC	SAND	SILT	CLAY
pH	1	−0.2937	0.6308	−0.0359	−0.3247	0.4991
OM	−0.2937	1	0.2463	−0.6761	0.6883	0.2205
CEC	0.6308	0.2463	1	−0.5641	0.0386	0.9068
Sand	−0.0359	−0.6761	−0.5641	1	−0.8089	−0.6086
Silt	−0.3247	0.6883	0.0386	−0.8089	1	0.0257
Clay	0.4991	0.2205	0.9068	−0.6086	0.0257	1

Discussion

Typically compounds with lower water solubility will have higher sorption coefficient values and will result in higher amounts of herbicide bound to the soil.[9] Pyroxasulfone is a unique compound in that it has very low water solubility (3.49 mg L^{-1} at 20°C), and yet has reduced soil binding compared to *s*-metolachlor and dimethenamid-*p*, which have higher water solubility values of 530 mg L^{-1} and 1450 mg L^{-1} at 20°C, respectively. Based solely on water solubility values, we hypothesized that pyroxasulfone would have the greatest sorption coefficient (K_d) value followed by *s*-metolachlor and then dimethenamid-*p*. However, when sorption coefficient studies were measured across 25 different soil types, we observe the trend of pyroxasulfone = dimethenamid-*p* < *s*-metolachlor in order of increasing soil binding. Average K_{oc} values listed in the WSSA Herbicide Handbook (9th Edition, 2007) for *s*-metolachlor (200 L kg^{-1}) and dimethenamid-*p* (55–125 L kg^{-1}) were similar to our average K_{oc} values of 268 and 149 L kg^{-1} for *s*-metolachlor and dimethenamid-*p*, respectively. Although there is little sorption coefficient data for dimethenamid-*p* in the literature, our data show that relative differences in adsorption between *s*-metolachlor and dimethenamid-*p* were similar to the listed K_{oc} values for these two compounds.

With all three herbicides, organic matter resulted in a significant correlation with herbicide soil adsorption. Generally, compounds with lower water solubility are adsorbed to a greater extent by organic matter.[10,11] This would explain why pyroxasulfone binding was highly correlated to organic matter (OM); however, results for all three herbicides indicate that herbicide adsorption was highly correlated to organic matter (>0.89 for all three herbicides) regardless of differences in their water solubility (Table 6). Generally, adsorption of a herbicide is positively correlated with its octanol–water partition coefficient and negatively correlated with the compounds' water solubility.[12] These herbicide characteristics appeared to predict the relative differences in soil binding between *s*-metolachlor and dimethenamid-*p*, but failed to predict the amount of soil binding for pyroxasulfone based on its water solubility and log K_{ow} (Table 6).

Table 5. Fisher's LSD grouping for all three herbicides across all soil types ($\alpha = 0.05$) LSD = 0.6179.

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT			
GROUPING	**MEAN**	***N***	**HERBICIDE**
A	4.01	25	*s*-Metolachlor
B	2.28	25	Dimethenamid-*p*
B	1.72	25	Pyroxasulfone

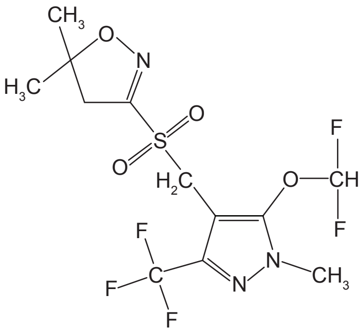
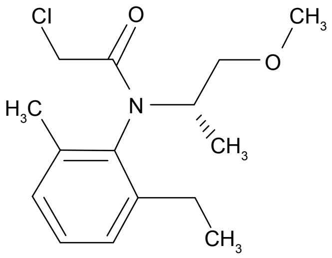
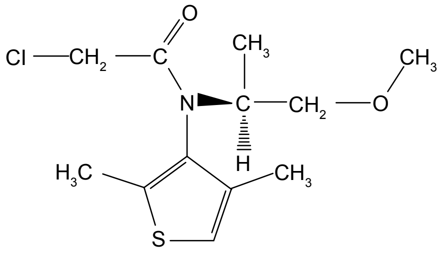
Notes: Groups with the same letter are not significantly different. Mean is the average K_d for each herbicide across all soils tested, and *N* is the number of soils tested for each herbicide.

In general within a group of structurally related compounds, the phytotoxicity of the herbicides of higher water solubility was less influenced by organic matter than that for those materials of lower water solubility.[10,11,13] Bailey et al[9] also concluded that within a chemically homologous series, the extent of adsorption was directly related to or governed by the compounds' water solubility. This would explain relative differences in adsorption between dimethenamid-*p* and *s*-metolachlor. It also shows the impact of differences in chemical structure and the influence of pyrazole- and chloroacetamide-based molecules on soil adsorption.

Weber et al[14] found that nonionizable organic herbicides generally bind to OM more readily than to other soil colloids such as clay minerals or metallic hydrous oxides. In their study, they showed that only two out of eight nonionizable herbicides K_d were correlated to clay minerals. Whereas all eight of the nonionizable herbicides tested were correlated to organic matter content.[14] Previous work with *s*-metolachlor has shown that soil retention was correlated to OM.[8,15,16] Others have shown that herbicide retention is correlated to both OM and clay content.[17–19] Weber et al[20] showed that K_d values were highly correlated with soil OM ($r = 0.97$), clay content ($r \geq 0.79$), and CEC ($r \geq 0.94$), although they did show a high correlation between percent clay and CEC ($r = 0.93$), which would explain their high correlation between K_d values and CEC. However, they did not list correlations between clay and OM for the soils tested, which could explain the correlation between sorption and clay content. Clay content and OM are typically correlated to each other since soils with higher clay content are typically more productive and tend to return more carbon into the system annually, which contributes to increased OM content over time.[21] In our study we observed a low correlation between OM and clay content ($r = 0.208$) and OM and CEC ($r = 0.25$) across all 25 different soil types (Table 6).

Although we did not have significant correlations to clay content or CEC, it is hard to say if correlations from previous literature were due to correlation between soil properties or if binding was actually correlated to these soil properties. For the 25 soil types used in our experiment, organic matter appeared to be the only soil property that was highly correlated to binding. Other soil properties and their correlation to herbicide binding could be explained by that soil properties correlation to organic matter. Our results are in agreement

Table 6. Chemical structure, chemical formula, water solubility, log K_{ow}, and vapor pressure values for pyroxasulfone, *s*-metolachlor, and dimethenamid-*p*.

	PYROXASULFONE	*s*-METOLACHLOR	DIMETHENAMID-*p*
			
Formula	$C_{12}H_{14}F_5N_3O_4S$	$C_{12}H_{22}ClNO_2$	$C_{12}H_{18}ClNO_2S$
Water solubility	3.49 mg L^{-1} @ 20°C	530 mg L^{-1} @ 20°C	1450 mg L^{-1} @ 20°C
Log K_{ow}	2.39	2.89	2.14
Vapor pressure	2.4×10^{-6} Pa @ 25°C	3.7×10^{-3} Pa @ 25°C	2.5×10^{-3} Pa @ 25°C

with previous authors, who found that OM was the main constituent for predicting binding. Results also differ from other previous reports that both OM and clay content were highly related to binding. Since we did not have a strong correlation between OM and either CEC or clay content, we can only conclude that OM was the dominant soil characteristic in terms of predicting herbicide binding.

Conclusion

Across all 25 soils evaluated, sorption coefficients indicate that pyroxasulfone had a lower degree of soil binding than dimethenamid-*p* and *s*-metolachlor, although pyroxasulfone behaved more similar to dimethenamid-*p*. Averaged across all soils evaluated, pyroxasulfone had the lowest average K_d value of 1.725 mg mL^{-1} while dimethenamid-*p* and *s*-metolachlor had higher average values of 2.278 mg mL^{-1} and 4.009 mg mL^{-1}, respectively. Results suggest that pyroxasulfone should be more available in the soil water solution than dimethenamid-*p* and *s*-metolachlor. Using a broad range of soils with diverse physical and chemical properties, statistical analysis suggests that organic matter correlates the best with herbicide binding for all three herbicides. Pearson correlations between sorption coefficient values and soil characteristics would support previous claims that pyroxasulfone activity under field conditions is inversely related to organic matter content.[22]

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Author Contributions

Conceived and designed the experiments: EPW and DLS. Analyzed the data: EPW. Wrote the first draft of the manuscript: EPW. Contributed to the writing of the manuscript: EPW, DLS, KB, RK. Agree with manuscript results and conclusions: EPW, DS, KB, RK. Jointly developed the structure and arguments for the paper: EPW. Made critical revisions and approved final version: DLS, KB, RK. All authors reviewed and approved of the final manuscript.

REFERENCES

1. Böger P, Matthes B, Schmalfuß J. Towards the primary target of chloroacetamides—new findings pave the way. *Pest Manag Sci*. 2000;56:497–508.
2. Stamper DM, Tuovinen OH. Biodegradation of the acetanilide herbicides alachlor, metolachlor, and propachlor. *Crit Rev Microbiol*. 1998;24:1–22.
3. Tanetani Y, Kaku K, Kawai K, Fujioka T, Shimizu T. Action mechanism of a novel herbicide, pyroxasulfone. *Pestic Biochem Physiol*. 2009;95:47–55.
4. Tanetani Y, Fujioka T, Kaku K, Shimizu T. Studies on the inhibition of plant very-long-chain fatty acid elongase by a novel herbicide, pyroxasulfone. *J Pestic Sci*. 2011;36:221–228.
5. Zollinger RK, Ries JL. *Sunflower Response to KIH-485*: National Sunflower Association Research Forum; 2007. Available from: http://wws.sunflowernsa.com/research workshop/documents/Zollinger_KIH_07.pdf. Accessed: March 29, 2012.
6. Pusino A, Liu W, Gessa C. Influence of organic matter and its clay complexes on metolachlor adsorption on soil. *Pestic Sci*. 1992;36:283–286.
7. Mueller TC, Steckel LE. Efficacy and dissipation of pyroxasulfone and three chloroacetamides in a Tennessee field soil. *Weed Sci*. 2011;59:574–579.
8. Obrigawitch T, Hons FM, Abernathy JR, Gipson JR. Adsorption, desorption, and mobility of metolachlor in soils. *Weed Sci*. 1981;29:332–336.
9. Bailey GW, White JL, Rothberg T. Adsorption of organic herbicides by montmorillonite: role of pH and chemical character of adsorbate. *Soil Sci Soc Am J*. 1968;32:222–234.
10. Carringer RD, Weber JB, Monaco TJ. Adsorption-desorption of selected pesticides by organic matter and montmorillonite. *J Agric Food Chem*. 1975;23:568–572.
11. Rahman A. Effect of soil organic matter on the phytotoxicity of soil-applied herbicides—glasshouse studies. *N Z J Crop Hortic Sci*. 1976;4:85–88.
12. Singh N, Kloeppel H, Klein W. Movement of metolachlor and terbuthylazine in core and packed soil columns. *Chemosphere*. 2002;47:409–415.
13. Weber JB, Weed SB. Effects of soil on the biological activity of pesticides1. In: Guenzi WD, editor. *Pesticides in Soil and Water*. Madison, WI: Acsess publication; 1974:223–256.
14. Weber JB, Wilkerson GG, Michael Linker H, et al. A proposal to standardize soil/solution herbicide distribution coefficients. *Weed Sci*. 2000;48:75–88.
15. Singh N, Kloeppel H, Klein W. Sorption behavior of metolachlor, isoproturon, and terbuthylazine in soils. *J Environ Sci Health B*. 2001;36:397–407.

16. Patakioutas G, Albanis TA. Adsorption—desorption studies of alachlor, metolachlor, EPTC, chlorothalonil and pirimiphos-methyl in contrasting soils. *Pest Manag Sci*. 2002;58:352–362.
17. Weber JB, Peter CJ. Adsorption, bioactivity, and evaluation of soil tests for alachlor, acetochlor, and metolachlor. *Weed Sci*. 1982;30:14–20.
18. Wood LS, Scott HD, Marx DB, Lavy TL. Variability in sorption coefficients of metolachlor on a Captina silt loam. *J Environ Qual*. 1987;16:251–256.
19. Weber JB, Swain LR. Sorption of diniconazole and metolachlor by four soils, calcium-organic matter and calcium-montmorillonite. *Soil Sci*. 1993;156:171–177.
20. Weber JB, McKinnon EJ, Swain LR. Sorption and mobility of 14C-labeled imazaquin and metolachlor in four soils as influenced by soil properties. *J Agric Food Chem*. 2003;51:5752–5759.
21. Burke et al. 1988.
22. Knezevic SZ, Datta A, Scott J, Porpiglia PJ. Dose-response curves of KIH-485 for preemergence weed control in corn. *Weed Technol*. 2009;23:34–39.