

## Metsulfuron Methyl Sorption–Desorption in Field-Moist Soils

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Pesticide sorption coefficients ( $K_d$ ) are generally obtained using batch slurry methods. As a consequence, the results may not adequately reflect sorption processes in field-moist or unsaturated soil. The objective of this study was to determine sorption of metsulfuron methyl, a weak acid, in field-moist soils. Experiments were performed using low density (i.e., 0.3 g mL<sup>-1</sup>) supercritical fluid carbon dioxide (SF-CO<sub>2</sub>) to convert anionic metsulfuron methyl to the molecular species and remove it from the soil water phase only, thus allowing calculation of sorption coefficients ( $K_d$ ) at low water contents.  $K_d$  values for sorption of the metsulfuron methyl molecular species on sandy loam, silt loam, and clay loam soil at 11% water content were 120, 180, and 320 mL g<sup>-1</sup>, respectively. Using neutral species  $K_d$  values, the  $pK_a$  of metsulfuron methyl, and the pH of the soil, we could successfully predict the  $K_d$  values obtained using the batch slurry technique, which typically has a predominance of anionic species in solution during the sorption characterization. This application of supercritical fluid extraction to determine sorption coefficients, combined with sulfonylureas'  $pK_a$  values and the soil pH, will provide an easy method to predict sorption in soil at different pH levels.

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**KEYWORDS:** Sorption; desorption; soil; sulfonylurea herbicides; metsulfuron methyl; sulfometuron methyl

### INTRODUCTION

An understanding of the binding mechanisms involved in the sorption of pesticides to soil can help us to understand and predict the behavior of pesticides in the soil system and, consequently, the potential risk for contamination of water resources. Pesticide sorption or binding in soil traditionally has been characterized by determining the partitioning of the pesticide between soil and solution resulting in pesticide sorption

coefficients ( $K_d$ ).  $K_d$  values are generally obtained using batch slurry methods that involve repeated shaking of the soil and centrifugation, which may alter the physical and chemical characteristics of the soil, resulting in changes in properties of the binding sites during the experiment. Therefore, partitioning of pesticides between solution and soil particles may not be the same in field-moist soils and batch slurry systems (1). As a consequence, the obtained batch  $K_d$  values may not adequately reflect sorption processes in field-moist or unsaturated soil.

A variety of techniques have been used to characterize pesticide sorption in field-moist or unsaturated soils. For

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**Table 1.** Physical and Chemical Properties of Minnesota Soils Used in This Study

	texture	organic carbon (%) <sup>a</sup>	clay (%) <sup>b</sup>	pH <sup>c</sup>
Webster	clay loam	4.1	35	6.7
Waukegan	silt loam	1.8	22	5.5
Verndale	sandy loam	1.4	7	6.1

<sup>a</sup> Determined by loss on ignition. <sup>b</sup> Determined by the hydrometer method. <sup>c</sup> Determined in 1:2 (w/w) soil:water.

instance, centrifugation techniques have been used to remove water for analysis from soils (2, 3). The sorption coefficients obtained for soils near field capacity differed from  $K_d$  values obtained under batch slurry conditions. Depending on the soil and chemical, both lower and higher sorption coefficients were obtained using the centrifugation method as compared to batch techniques. On the basis of these results, the authors questioned the validity of applying sorption coefficients obtained with batch slurry methods to field-moist soils.

The selectivity of supercritical fluid extraction (SFE) has recently been used for characterization of soil–pesticide interactions and calculation of sorption coefficients ( $K_d$ ) in field-moist soils (4–6). This method has numerous advantages. For instance, it excludes mechanical laboratory steps, such as shaking and centrifugation, which in turn minimizes the risk for potential changes in the properties of the sorptive sites. Also, sorption–desorption experiments can be performed in short time periods, which minimizes effects due to pesticide decomposition. Effects of temperature and soil moisture content can also easily be determined. While a quick and easy technique, the SFE method has limitations. For instance, to use the SFE method to determine  $K_d$ , an appropriate supercritical fluid (i.e., SF-CO<sub>2</sub>) and density, which removes pesticide from soil solution only, is essential (6). Because of the low amounts of pesticide in the small volume of soil solution, the use of radiolabeled compounds throughout the experiments is generally necessary to facilitate analyses and mass balance calculations.

Thus far, the SFE method has only been used to characterize sorption in field-moist soils for three classes of pesticides: triazines (atrazine) (4–6), azoles (triadimefon) (7), and phenylureas (linuron) (8). The objective of this study was to use SFE to determine sorption of metsulfuron methyl, a sulfonylurea (SU) herbicide, in field-moist soils and to compare the results with batch slurry techniques.

## MATERIALS AND METHODS

**Chemicals and Soils.** Metsulfuron methyl (methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate) (>99% purity), sulfometuron methyl (methyl 2-[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate) (>99% purity), <sup>14</sup>C uniformly ring-labeled metsulfuron methyl ( $1.4 \times 10^9$  Bq g<sup>-1</sup>), and sulfometuron methyl ( $1.8 \times 10^9$  Bq g<sup>-1</sup>) were supplied by DuPont Agricultural Products (Wilmington, DE). SFE grade CO<sub>2</sub> was obtained from Air Products and Chemicals, Inc. (Allentown, PA). Pesticide grade methanol and CaCl<sub>2</sub> were obtained from Fisher Scientific (Fair Lawn, NJ). Ecolite scintillation cocktail (ICN, Costa Mesa, CA) was combined with SF-CO<sub>2</sub> extracts for <sup>14</sup>C quantification by liquid scintillation counting (LSC). Three Minnesota surface (0–15 cm) soils, a Webster clay loam (Typic Haploquoll), a Verndale sandy loam (coarse loamy over sandy, mixed frigid Udic Argiboroll), and a Waukegan silt loam (fine silty over sandy or sandy skeletal, mixed mesic Typic Hapludoll), were used in this study. Selected physical and chemical properties of the soils are listed in Table 1.

**Sample Preparation.** Subsamples of field-moist soils (5.0 g) were weighed into aluminum weighing boats and treated with <sup>14</sup>C-labeled

metsulfuron methyl ( $5.5 \times 10^3$  Bq mL<sup>-1</sup>) solution in methanol (1 mL,  $19 \mu\text{g mL}^{-1}$ ), to give a final concentration of  $4 \mu\text{g g}^{-1}$  soil (dry weight basis). Original soil moisture contents were determined after 24 h at 105 °C. Although this concentration is 40 times greater than the maximum application rate (assuming uniform incorporation in the surface 2.5 cm of soil), it facilitates comparison of data between this experiment and the batch sorption experiment. Assuming that all of the chemical is sorbed, the sorbed concentration would be the same as the sorbed concentration in the middle of the batch sorption isotherm (see Batch Sorption Experiment section).

After the soils were mixed with the spike solution, ~0.5 mL of water was added to the soils, and the soils were then allowed to dry at room temperature (~23 °C) to their original weights to ensure removal of methanol. For a comparative study at 17% water content, additional deionized water was added to the spiked soil in the weighing boats (after evaporation of methanol) and mixed thoroughly. The soil was weighed into the extraction thimbles and equilibrated 24 h before extraction. Sulfometuron methyl was spiked only on the Waukegan silt loam soil using the same procedure and herbicide concentration. Soil samples were prepared in duplicate.

**SFE Sorption Experiments.** SF-CO<sub>2</sub> sorption experiments were conducted using a HP7680A supercritical fluid extractor (Hewlett-Packard, Little Falls, DE), described earlier (5). The soil in the extraction thimble was swept with 30.8 mL of CO<sub>2</sub> at 0.30 g mL<sup>-1</sup> density (4.4 thimble volumes). Ten 5 min sequential sweep periods were utilized for each sample. Between sequential sweep periods, 7 min elapsed during depressurization, rinsing of the cryotrap, and weighing of the sample vessel to determine water losses. The 7 min periods are considered desorption equilibrations, and water contents at each equilibration were used in the  $K_d$  calculations. Thimble, trap, and nozzle temperatures were 40, 10, and 55 °C, respectively. The trap was rinsed twice after extraction with 1.4 mL of methanol into two empty vials.

Each SFE extract was then combined with scintillation cocktail, and the radioactivity was determined by LSC using a Packard 1500 Tri-carb Liquid Scintillation Analyzer (Downers Grove, IL) (more than 95% of the extracted analyte was found in the first vial). Mass balances of <sup>14</sup>C were determined by combusting triplicate subsamples (0.3 g) of the extracted soil, which had been mixed with an equal volume of microcrystalline cellulose powder, using a Packard 306 sample oxidizer and quantifying the released <sup>14</sup>CO<sub>2</sub> by LSC. Average mass balances of metsulfuron methyl and sulfometuron methyl for soils before and after SF-CO<sub>2</sub> extraction were  $99 \pm 5\%$ , indicating that essentially all of the metsulfuron methyl and sulfometuron methyl applied to the soil was recovered from the trap or was still sorbed to the soil.

Sorption coefficients after the initial equilibration,  $K_d$ -SE, were calculated from  $K_d = [C_s]/[C_w]$ , where  $[C_w]$  is the soil water phase concentration determined by the amount of metsulfuron methyl and sulfometuron methyl in the SFE extract divided by the amount in water in the soil and  $[C_s]$  is the concentration of metsulfuron methyl and sulfometuron methyl sorbed to soil determined by the difference between the initial amount of chemical added to soil and the amount of chemical in the SFE extract after equilibration divided by the amount of dry soil. Desorption coefficients ( $(K_d - (D1 - D9))$ ) (nine desorption equilibrations) were calculated in a similar manner, except when calculating the sorbed concentration; the total amount of chemical in the system was reduced by the amount of chemical removed in previous SFE steps. Water contents at each equilibration were used in the calculations.

**Batch Sorption Experiments.** Batch sorption–desorption experiments were performed by weighing 10 g soil samples (air-dried) into 25 mL glass centrifuge tubes and adding 10 mL of <sup>14</sup>C-metsulfuron methyl solution prepared with 0.01 M CaCl<sub>2</sub>. Initial <sup>14</sup>C-metsulfuron methyl solution concentrations were 0.5, 1.4, 2.0, 5.6, 20, and 56  $\mu\text{g mL}^{-1}$ . The soil slurries were sealed with Teflon-lined caps and shaken at  $23 \pm 2$  °C for 24 h and then centrifuged at 1000 rpm for 30 min. Preliminary studies showed that equilibrium was attained in less than 24 h and that there was no sorption onto the centrifuge tubes. The supernatant (5 mL) was removed, and a 1 mL aliquot was counted by LSC. Desorption experiments were performed using samples from initial metsulfuron methyl solutions of 2–56  $\mu\text{g mL}^{-1}$ . After 5 mL of supernatant solutions were removed from sorption experiments, solu-

tions of 0.01 M CaCl<sub>2</sub> without metsulfuron methyl were weighed into the tubes to obtain slurries of 10 mL of solution to 10 g of soil. At each desorption step, the soil in the tubes was resuspended in solution using a vortex mixer. The tubes were capped and shaken for 24 h. A total of three 24 h desorption equilibration steps were performed.

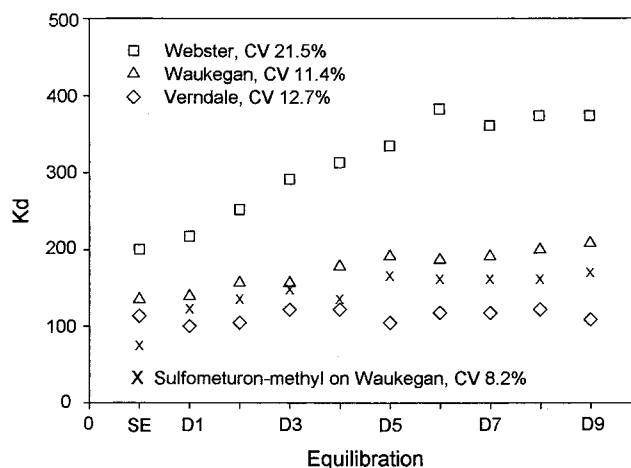
Sorption Freundlich  $K_f$  and  $1/n$  values were calculated using the Freundlich equation, which has the general formula  $x/m = K_f C^{1/n}$ , where  $x/m$  is the concentration of herbicide on the soil (difference between initial metsulfuron methyl concentration and concentration after equilibration was assumed to sorbed on the soil,  $\mu\text{g g}^{-1}$ );  $K_f$  is the Freundlich sorption coefficient;  $C$  is the concentration of herbicide in the soil solution after equilibration ( $\mu\text{g mL}^{-1}$ ); and  $1/n$  is the slope of the sorption isotherm. The equation, rewritten as  $\log x/m = \log K_f + 1/n \log C$ , was used for plotting isotherms.

## RESULTS AND DISCUSSION

**SFE Sorption Method.** Pesticides exist in two phases in soil, sorbed on soil surfaces and in solution around soil particles. The developed SFE technique to measure pesticide sorption in unsaturated soils is based on the assumption that the pesticide is extracted from the soil water phase only and not from the soil and that this can be done by adjusting the SF-CO<sub>2</sub> density. The solvent strength of a supercritical fluid is directly related to its density; the solvent strength of the SF-CO<sub>2</sub> increases with density. If we also assume that at least two equilibria exist in the SFE system, a slow sorption–desorption equilibrium between pesticide in the soil and pesticide in the water phase and a very fast equilibrium between pesticide in the water phase and pesticide in the supercritical fluid, we can avoid extraction of soil-sorbed pesticide by using mild extraction conditions with low density SF-CO<sub>2</sub> (0.30 g mL<sup>-1</sup>). The SFE method has been used to successfully characterize sorption in field-moist soils for atrazine (4–6), triadimefon (7), and linuron (8), using low density SF-CO<sub>2</sub>. Increased SF-CO<sub>2</sub> density significantly underestimated  $K_d$  values because extracted pesticide was assumed to be in the solution.

Because the described method is based on extraction of pesticides from the soil water phase only and not from soil, mild extraction conditions (low SF-CO<sub>2</sub> density, 0.30 g mL<sup>-1</sup>; short extractions times, 5 min) were used to extract all of the metsulfuron methyl and sulfometuron methyl in the solution surrounding the soils, while avoiding extraction of soil-sorbed metsulfuron methyl and sulfometuron. At low density, there is a potential concern that not all of the pesticide is extracted from the soil water solution due to low solubility of the pesticide in the SF-CO<sub>2</sub>. In a preliminary study (unpublished), extraction of a loamy sand soil with 0.5% organic carbon (OC) content at 0.30 g mL<sup>-1</sup> yielded much higher concentrations of metsulfuron methyl and sulfometuron in the SF-CO<sub>2</sub> than extractions of the silt loam and clay loam soils, indicating that the SF-CO<sub>2</sub> was not saturated with metsulfuron methyl and sulfometuron during our experiments.

While it seems unlikely that the mild conditions (i.e., low SF density) used in this study would extract any soil-bound pesticide, unfortunately, there is no suitable method to measure the trace amounts of metsulfuron methyl that may have been extracted from the soil under these conditions. It should be noted that much harsher conditions (i.e., SF-CO<sub>2</sub> density = 0.9 g mL<sup>-1</sup>, 2% methanol modifier, 30 min extraction) were required for quantitative extraction (85%) of metsulfuron from these same soils (9). Also, additional experiments showed that high density SF-CO<sub>2</sub> (0.9 g mL<sup>-1</sup>) moved metsulfuron methyl along the direction of SF-CO<sub>2</sub> flow comparable to chromatography. After 15 min, higher amounts of metsulfuron methyl were found at the top of the thimble than at the bottom. This further indicates



**Figure 1.** Metsulfuron methyl sorption–desorption coefficients ( $K_d$ ) for SE and desorption equilibrations (D1–D9) for Webster, Waukegan, and Verndale soils at 11% soil moisture contents. Also shown is the sulfometuron sorption–desorption profile for Waukegan soil.

a continuous equilibrium process for the pesticide between the soil and the soil water phase.

The relatively constant  $K_d$  values for the desorption equilibria D1–D9 for Waukegan and Verndale soils (Figure 1) also strongly suggest that metsulfuron methyl and sulfometuron methyl were strongly sorbed and not extractable from the soil. If metsulfuron methyl and sulfometuron methyl were extracted from the soil, the amounts attributed to the solution phase would decrease with an increased number of desorption equilibrations as the metsulfuron methyl and sulfometuron methyl were removed from the more labile sites, which in turn would result in a large increase in  $K_d$ , which was not the case.

To characterize sorption–desorption in field-moist soils, the water contents must remain the same during the experiment. The solubility of water in SF-CO<sub>2</sub> is dependent on the SF-CO<sub>2</sub> density; the solubility of water in SF-CO<sub>2</sub> increases with increases in SF-CO<sub>2</sub> density. Therefore, at high density, the soil moisture content would change during the experiment, but the solubility of water in low density SF-CO<sub>2</sub> would be minimal. At a SF-CO<sub>2</sub> density of 0.30 g mL<sup>-1</sup>, there was only a 2% decrease in water content from the samples during the course of the experiment (10 5 min sweep periods). Thus, very little water entered the supercritical fluid, and both SF-CO<sub>2</sub> and liquid water were expected to be present during all experiments, hence maintaining equilibrium in the system.

Only a small amount of metsulfuron methyl, usually less than 0.1% of the initial in the system, was removed during each equilibration step. Therefore, the original equilibrium was only slightly altered and could return to equilibrium very rapidly, within the 7 min desorption equilibration period. Extending the extraction time from 5 to 30 min increased the amount extracted (Webster soil, from 0.06 to 0.25% recovery), indicating the existence of a continuous equilibrium process between pesticide sorbed to the soil and pesticide sorbed in the water phase. These results strongly indicate the existence of a soil–soil water–SF-CO<sub>2</sub> equilibrium, well-suited for calculations of sorption coefficients at low water contents, and the experimental setup and SFE conditions used were sufficient to reach and maintain this equilibrium.

**Effect of Soil Properties.** Profiles of sorption and desorption (D1–D9) equilibrations obtained for metsulfuron methyl on Webster, Waukegan, and Verndale soils and sulfometuron methyl on Waukegan soil at 11% soil moisture are shown in



**Figure 1.** The 24 h period after spiking of the sample is considered the sorption equilibration (SE). The 7 min periods between the sequential sweep periods are the desorption equilibration periods (D1–D9). Metsulfuron methyl  $K_d$  SE for the Webster, Waukegan, and Verndale soils were 210, 140, and 120, respectively. Calculated  $K_d$  values increased through nine desorption equilibrations (D1–D9) for the Webster soil (220–380) and were significantly higher than those for the Waukegan (140–210) and Verndale soils (120, relatively constant). Average  $K_d$  values for all sorption and desorption equilibrations (of SE and D1–D9) in Webster, Waukegan, and Verndale soils were 320, 180, and 120, respectively.

$K_d$  increased for the Webster and Waukegan soils with each consecutive desorption equilibration step. This is probably due to the removal of more readily desorbable metsulfuron methyl, similar to a hysteresis effect in batch slurry experiment, in which strongly sorbed metsulfuron methyl does not desorb into solution during desorption equilibrations.

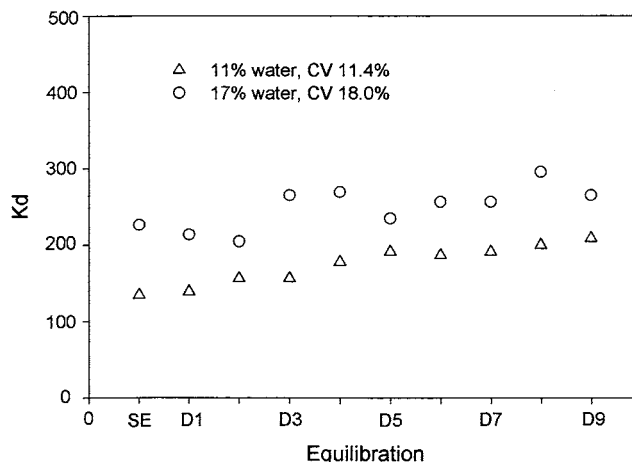
The average coefficients of variation (CV) for metsulfuron methyl were as follows: 21.5%, Webster soil; 11.4%, Waukegan soil; and 12.7%, Verndale soil. In general, as sorption,  $K_d$ , increased from SE to D9, CV increased. The greater error in  $K_d$  at higher sorption is due to decreased precision in measuring the small changes in the amounts of herbicide in solution (10).

To compare metsulfuron methyl sorption–desorption on the three soils, desorption coefficients  $K_d$  D1 for Webster (220), Waukegan (140), and Verndale (100) soils were used. Relative linear relationships between  $K_d$  D1, for metsulfuron methyl at 11% soil moisture contents, and OC content ( $K_d$  D1 = 31.1 (% OC) + 53.2,  $r^2 = 0.962$ ) and clay content ( $K_d$  D1 = 4.24 (% clay) + 62.8,  $r^2 = 0.947$ ) were obtained. Correcting sorption  $K_d$  values for OC content ( $K_{oc}$  D1 = ( $K_d$  D1/% OC)  $\times$  100) for Webster, Waukegan, and Verndale soils,  $K_{oc}$  D1 values were 5400, 7800, and 7100, respectively. No correlation was found between sorption and soil pH.

The sorption–desorption profile obtained for sulfometuron methyl on Waukegan soil shows a profile and  $K_d$  values similar (average  $K_d$  value = 150) to those for metsulfuron methyl (Figure 1). With sulfometuron methyl,  $K_d$  increased from 80 ( $K_d$  SE) to 180 ( $K_d$  D9), and  $K_d$  D1 = 120 and  $K_{oc}$  D1 = 6700, also similar to metsulfuron methyl. The average CV for sulfometuron methyl on Waukegan silt loam soil was 8.2%.

SU herbicides are weak acids; therefore, sorption on soil is basically a function of pH and soil OC and clay contents (11). The neutral species of SUs would be sorbed, while the anion would be repelled by the soil surface or only slightly sorbed. Thus, sorption would be expected to be greater at low pH and high OC and clay contents and lower at high pH and low OC and clay contents, with pH the most important factor. A previous study with metsulfuron methyl showed a high correlation between sorption and soil pH and OC, but the correlation with OC was lost when two soils of very high organic content (26 and 35%) were excluded from the correlation, leaving OC of 1.6–5.0%, while the correlation with pH was affected only slightly (12). Results from studies on sulfometuron methyl sorption show no correlation between batch sorption and OC content (13, 14).

Sorption of metsulfuron methyl with a  $pK_a$  value of 3.3 would be expected to be much greater than for sulfometuron methyl ( $pK_a = 5.5$ ) due to the higher percentage of neutral species in the soil solution. However, the SFE results showed a similar sorption–desorption profile (Figure 1), with metsulfuron methyl being sorbed to only a slightly greater extent. This would be expected due to similarities in structure between sulfometuron



**Figure 2.** Effect of moisture on SFE  $K_d$  values for metsulfuron methyl on Waukegan soil.

methyl and metsulfuron methyl, only if there were no pH–sorption interactions. None of the three soils in the present study are particularly acidic (pH 5.5–6.7); however, water in contact with SF-CO<sub>2</sub> has a pH of just below 3, due to formation of carbonic acid (15). Thus, the SUs would be predominantly neutral species in all three soils and differences in sorption would be attributed to differences in OC and clay contents, as was observed on these soils, and not soil pH. It should also be remembered that only neutral SU would be partitioned into SF-CO<sub>2</sub>; anions are not soluble in SF-CO<sub>2</sub>.

**Effect of Water Content.** Increasing the water content from 11 to 17% significantly increased metsulfuron methyl sorption in Waukegan silt loam soil (Figure 2). For instance,  $K_d$  D1 on the silt loam soil increased from 140 to 220 when water content increased from 11 to 17%. Relatively constant  $K_d$  values (CV of 11 and 18%) were obtained at both water contents for the SE through nine desorption equilibrations (D1–D9), indicating the desorption equilibrium at both water contents was reestablished very rapidly, within the 7 min that it took to depressurize the system and weigh the thimble.

Increased sorption with increased water content have been observed with atrazine (4, 5) and linuron (8). The reason for the increase in  $K_d$  with increased water content from 11 to 17% is not entirely understood. One explanation may be that higher water contents facilitate greater accessibility to more strongly sorbing sites on pore walls. Another explanation could be inefficiency in SF-CO<sub>2</sub> extraction of water in soil pores. Lower SFE recoveries with increasing water content were reported earlier (16, 17). Water can shield the matrix and act as a barrier to CO<sub>2</sub> penetration into small pores (16).

**Batch Slurry Method.** Batch sorption–desorption data for metsulfuron methyl fit the Freundlich equation on all three soils (Table 2, Figure 3). Isotherm slopes ( $1/n_{\text{sorption}}$ ) for Webster and Verndale soils were significantly  $<1.0$ , indicating that sorption is concentration-dependent. Sorption of metsulfuron methyl on the Waukegan soil was not concentration-dependent. Because  $1/n_{\text{sorption}}$  values were not equal,  $K_f$  values cannot be statistically compared. However, for comparative purposes, sorption  $K_f$  values increased in the following order: Verndale  $<$  Waukegan  $<$  Webster soil. A relative linear relationship between  $K_f$  and clay content ( $r^2 = 0.927$ ) was obtained; however, correlation with OC was worse ( $r^2 = 0.584$ ), while no correlation with pH was found.

Desorption isotherms slopes,  $1/n_{\text{desorption}}$ , were lower than  $1/n_{\text{sorption}}$  (Figure 3, Table 2), indicating desorption hysteresis

Table 2. Batch Metsulfuron Methyl Sorption and Desorption Characterization on Three Soils

soil type	initial concn ( $\mu\text{g mL}^{-1}$ )	$K_f$	$K_{foc}$	$1/n_{\text{sorption}}$	$r^2$	$1/n_{\text{desorption}}$	$r^2$
Webster clay loam	0.5–56	0.41 (0.38–0.44) <sup>a</sup>	10 (9–11)	0.85 ( $\pm 0.03$ )	0.99		
	56					0.29 ( $\pm 0.02$ )	0.99
	20					0.26 ( $\pm 0.01$ )	0.99
	5.6					0.21 ( $\pm 0.01$ )	0.99
	2					0.21 ( $\pm 0.04$ )	0.94
Waukegan silt loam	0.5–56	0.36 (0.32–0.40)	20 (18–20)	1.01 ( $\pm 0.04$ )	0.99		
	56					0.26 ( $\pm 0.01$ )	0.99
	20					0.17 ( $\pm 0.07$ )	0.77
	5.6					0.18 ( $\pm 0.03$ )	0.94
	2					0.15 ( $\pm 0.02$ )	0.97
Verndale sandy loam	0.5–56	0.18 (0.16–0.20)	13 (11–14)	0.74 ( $\pm 0.03$ )	0.99		
	56					0.69 ( $\pm 0.05$ )	0.99
	20					0.48 ( $\pm 0.16$ )	0.82
	5.6					0.52 ( $\pm 0.10$ )	0.94
	2					0.53 ( $\pm 0.06$ )	0.97

<sup>a</sup> Number in parentheses is standard error about the mean.

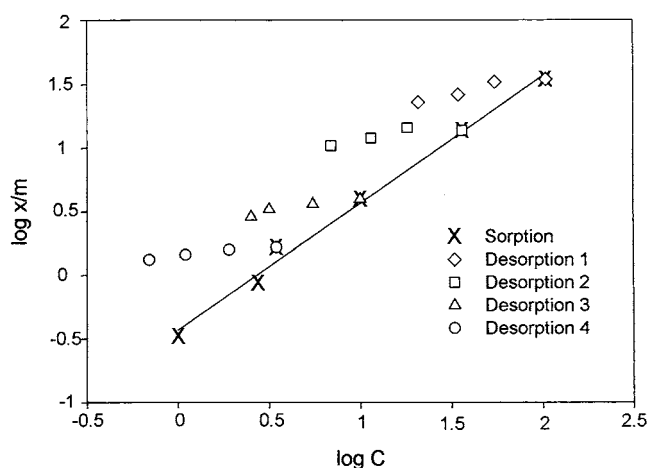
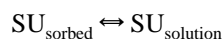


Figure 3. Metsulfuron methyl batch sorption and desorption isotherms on Waukegan silt loam soil. Desorption 1–4 refers to desorption from soil initially equilibrated with solutions of 56, 20, 5.6, and 2.0  $\mu\text{g mL}^{-1}$ , respectively.

for all soils. The greater hysteresis observed in the Webster and Waukegan soils, as compared to Verndale soil, was similar to effects observed with the SFE technique.

**Comparison of SF-CO<sub>2</sub> and Batch Methods.** The same order of increasing metsulfuron methyl sorption in Verndale, Waukegan, and Webster soils in both the field-moist soil and the batch slurry soil methods (Figure 1, Table 2) was observed. However,  $K_d$  values determined by the SFE method in field-moist soil were  $\sim 500$  times greater than  $K_f$  values obtained in the batch slurry soil. The greater sorption determined by the SFE method as compared to the batch system is that in the SFE method, the sorption coefficient is for the sorption of the neutral species on soil. At the pH of the SF-CO<sub>2</sub> water system (pH < 3), SUs in solution are the neutral species and the equilibrium being characterized is



In contrast, in the batch system, the solution pesticide concentration is measured in the bulk 0.01 M CaCl<sub>2</sub> solution; therefore, the contribution of the anion to the calculation of  $K_d$  becomes important. The batch system equilibrium would be



Assuming only neutral species are sorbed and using the  $K_d$  for the neutral species, the  $\text{p}K_a$  and the soil pH, we can calculate a predicted batch  $K_d$  for the soils with the following equation:

$$K_{d-\text{batch}}(\text{SU}) = f_{\text{SU}}(K_{d-\text{SFE}}(\text{SU})) + (1 - f_{\text{SU}})(K_{d-\text{SFE}}(\text{SU}^{-}))$$

where  $K_{d-\text{batch}}(\text{SU})$  is the batch SU sorption coefficient,  $f_{\text{SU}}$  is the fraction of the SU in the neutral species ( $f_{\text{SU}} = 1/(1 + 10^{\text{pH}-\text{p}K_a})$ ),  $K_{d-\text{SFE}}(\text{SU})$  is the SFE measured SU (neutral species) sorption coefficient, and  $K_{d-\text{SFE}}(\text{SU}^{-})$  is the sorption coefficient of the SU anion. Calculated batch sorption coefficients for metsulfuron methyl on the three soils, Webster  $K_{d-\text{batch}} = 0.23$ , Waukegan  $K_{d-\text{batch}} = 1.12$ , and Verndale  $K_{d-\text{batch}} = 0.19$ , generally agreed with the measured batch  $K_f$  values (Table 2).

## CONCLUSIONS

The described application of SFE to determine sorption coefficients of the neutral species of a SU herbicide provides a better overall perspective of SU fate in the field than does sorption characterized by the batch slurry method. For instance, when combined with the  $\text{p}K_a$  and pH of given soils, we can predict the sorption coefficient for the soils. While the described method will work for metsulfuron methyl and sulfometuron methyl, the method is not applicable to all SUs, i.e., nicosulfuron cannot be extracted from soils by SFE (9). It should be possible to extend this SFE method further to give more information about sorbing sites with different sorptive strengths and to other weak acid herbicides.

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