Partitioning of Penoxsulam, a New Sulfonamide Herbicide

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Penoxsulam (trade name Granite) is a new acetolactate synthase (ALS) inhibitor herbicide for postemergence control of annual grasses, sedges, and broadleaf weeds in rice culture. This study was done to understand the equilibrium phase partitioning of penoxsulam to soil and air under conditions simulating California rice field conditions. Partitioning of penoxsulam was determined between soil and water (K_d) by the batch equilibrium method and between air and water (K_H) by the gas-purge method. In four representative soils from the Sacramento Valley, the K_d values ranged from 0.14 to 5.05 and displayed a modest increase with soil pH. In soil amended with manure compost, soil sorption increased 4-fold with increasing soil organic matter content, but was still low with a K_d of 0.4 in samples with high organic carbon contents of 15%. Penoxsulam was confirmed to be extremely nonvolatile and did not partition into air at any measurable rate at 20 or 40 °C. K_H (pH 7) was estimated at 4.6×10^{-15} Pa·L·mol^{-1} on the basis of available water solubility and vapor pressure data. The results imply that soil and air partitioning of penoxsulam do not significantly affect its potential for degradation or offsite movement in water.

KEYWORDS: Environmental mobility; Granite; penoxsulam; sulfonamide; adsorption; partitioning; sorption value; soil pH

INTRODUCTION

Penoxsulam is the active ingredient of Granite (trademark of Dow AgroSciences LLC), a new herbicide designed for postemergence control of annual grasses, sedges, and broadleaf weeds in rice culture (*1*). It has received a reduced risk designation by the United States Environmental Protection Agency (USEPA) (*2*), conditional registration in September 2004 (*3*), and is scheduled for release in 2005 (*4*).

Penoxsulam is a triazolopyrimidine sulfonamide and belongs to an herbicide group called ALS (acetolactate synthase) inhibitors (*1*). ALS is an enzyme needed for the biosynthesis of the branched-chain amino acids and is found in plants, fungi, and bacteria, but not mammals (*5*). Accordingly, penoxsulam is not expected to pose a threat to aquatic or terrestrial mammals or humans. However, some of the risk quotients (RQs) obtained in screenings of aquatic and terrestrial plants exceeded levels of concern and raise the possibility that penoxsulam applications may harm certain endangered plants if not appropriately managed (*2*).

To estimate the exposure risks of penoxsulam in different management scenarios for the rice field environment and tailwaters, adequate quantitative information in the form of partition constants and degradation rates is required. However, there is little available data on the environmental fate and effects of penoxsulam. Therefore, the main objective of this study was
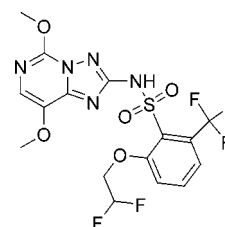

Figure 1. Chemical structure of penoxsulam.

to determine the soil—water and air—water partition constants of penoxsulam and to evaluate the most important factors affecting its partitioning behavior.

MATERIALS AND METHODS

Chemicals and Soils. Penoxsulam (2-(2,2-difluoroethoxy)-*N*-(5,8-dimethoxy[1,2,4]triazolo[1,5-*c*]pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide; purity, 98.8% active ingredient) (**Figure 1**) and [^{14}C]penoxsulam (*N*-((1-(2,2-difluoroethoxy)-3-trifluoromethyl-2-benzene)sulfonyl)-2-amino-5,8-dimethoxy[1,2,4]triazolo[1,5-*c*]pyrimidine-2-^{14}C; 28.1 mCi/mol) were supplied by Dow AgroSciences LLC (Indianapolis, IN). Roberts et al. (*1*) report pH-dependent water solubilities for penoxsulam of 5.7 mg L^{-1} at pH 5, 410 mg·L^{-1} at pH 7, and 1460 mg·L^{-1} at pH 9 and a vapor pressure of 9.5×10^{-14} Pa at 25 °C. Stock solutions were prepared in acetonitrile. Work solutions were prepared in 0.01 M CaCl$_2$ buffer to avoid the inclusion of solvents in the test systems (*6*). This is feasible due to the relatively high water solubility of penoxsulam. All stock solutions contained 200 mg L^{-1} Hg(II)Cl$_2$ to prevent microbial degradation (*7*).

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Table 1. Selected Properties of Rice Soils and Manure Compost

soil name	texture	collection site	silt (%)	clay (%)	sand (%)	OC (%)	OM (%)	pH	CEC (mequiv/ 100 g)
Sacramento	clay	Schiedel Ranch 39°18′41N, 122°10′41W	34	40	26	1.33	2.29	6.5	38.7
San Joaquin	loam	Matthews Ranch 39°13′09N, 121°32′46W	43	20	37	0.5	0.86	5.3	12.7
Stockton	clay adobe	Thompson Ranch 39°31′22N, 121°55′46W	33	50	17	0.74	1.28	4.6	37.7
Willows	clay	Maxwell–Dennis Ranch 39°18′41N, 122°10′41W	48	37	15	1.12	1.93	6.8	34.8
manure						24.8	42.6	7.7	

The soil sorption potential of penoxsulam was evaluated for the four soils most commonly used for rice cultivation in the Sacramento Valley: Sacramento clay, San Joaquin loam, Stockton clay adobe, and Willows clay. Taxonomically, Sacramento clay is classified as a fine, montmorillonitic, noncalcareous, thermic Cumulic Haplaquoll (*8*); San Joaquin loam as a fine, mixed, thermic Abruptic Durixeralf (*9*); and Stockton clay adobe and Willows clay as fine, montmorillonitic, thermic Typic Pelloxererts (*9*). Soil samples were collected from the top 20 cm layer of representative locations on April 27, 2004 (San Joaquin loam) and on May 7, 2004 (Sacramento clay, Stockton clay adobe, Willows clay). Soils were oven-dried (100 °C), disaggregated via hammering, and homogenized using a mortar and pestle. Larger pieces of plant material were removed with forceps and the soils were sieved to a particle size ≤1.4 mm. Compost made of steer manure and plant material (Ace Organic Steer Manure; Ace, Oak Brook, IL) was also passed through a 1.4 mm sieve prior to use. To study the effect of organic matter on sorption, Willows clay was amended with the compost at 10, 20, and 60% (w/w; dry weight). Willows clay was also oxidized with 30% H_2O_2 (90 °C, three times) to remove native organic matter, and the oxidized soil was used for sorption measurements (*10*). To study the effect of pH, San Joaquin loam and Willows clay were equilibrated with buffer solution titrated with HCl and NaOH to yield an initial pH ranging between 2 and 9. The processed soil samples and compost were kept at 5 °C in the departmental cold storage room before experimental use.

The physicochemical properties of the soils were determined by the Division of Agriculture and Natural Resources Analytical Laboratory (DANR Lab) at UCD and are summarized in **Table 1**. Soil composition (sand/silt/clay) was determined by particle size analysis (*11*). Soil pH was measured from a saturated soil paste extract (*12*). The soil organic carbon and organic matter contents were determined by the Walkley–Black method (*13*). The cation exchange capacity (CEC) was determined by barium acetate saturation and calcium replacement (*14*).

Air–Water Partitioning. The Henry's law constant (air–water partitioning constant) K_H was calculated according to $K_H = P^0/S$. We also attempted to measure the Henry's law constant K_H with the gas-purge method (*15*). In this method, an inert gas (e.g. ultrapure nitrogen) is bubbled at a known flow rate through a solution with the chemical in question, and the decrease in the solution phase concentration is monitored over time. The Henry's law constant K_H can be determined according to the expression $K_H = -kVRT/G$, where k is the first-order dissipation rate constant (s^{-1}), V is the solution volume (m^3), and G is the nitrogen flow rate (m^3·s^{-1}). K_H can be converted into the dimensionless Henry's law constant $K_H' = K_H/RT$.

The custom-made gas-purge apparatus consisted of two jacketed, temperature-controlled Pyrex cylinders containing 1 L of a 12 mg L^{-1} penoxsulam solution in 0.01 M CaCl$_2$ and 200 mg L^{-1} Hg(II)Cl$_2$. Glass tube inserts tipped with coarsely fritted disks near the bottom of the vessel bubbled a constant nitrogen stream through the solution for 48 h at a flow rate of 1000 mL min^{-1}. The experiment was conducted in duplicate at 20 and 40 °C. At certain time intervals, 1-mL duplicate samples of the aqueous solution were withdrawn and transferred to amber 2-mL autosampler vials. Penoxsulam concentrations were

measured by liquid chromatography–tandem mass spectroscopy (LC/MSMS, see below) (*1*).

Chemical Analysis. Analysis was based on a modified procedure developed previously by Dow AgroSciences LLC (*1*) and involved an Agilent Model 1100 LC system (Palo Alto, CA) and an API 2000 MS/MS (MDS Sciex, South San Francisco, CA). The column was a Luna 3 μm C-8 (Phenomenex, Torrence, CA). The mobile phase was 50:50:0.01 acetonitrile:methanol:acetic acid (phase A) and 100:0.01 water:acetic acid (phase B). For elution of penoxsulam, the following elution gradient was used at a flow rate of 150 μL min^{-1} with a total run time of 20 min: start (0 min, 30:70 phase A:B), step 1 (1 min, 100:0), step 2 (8 min, 100:0), step 3 (8.1 min, 30:70), step 4 (20 min, 30:70). Analysis for penoxsulam was performed in positive ionization mode with an electrospray interface. The injection temperature was 450 °C. The Q1/Q3 ions for penoxsulam were 484/195.

Soil–Water Partitioning. Soil slurries were prepared consisting of radiolabeled penoxsulam solutions at known concentrations in 0.01 M CaCl$_2$ and soil samples of known dry weight. Radiolabeled solutions of penoxsulam were prepared by adding [^{14}C]penoxsulam (0.03 mg·L^{-1} ≈ 4000 cpm·mL^{-1}) to solutions containing unlabeled penoxsulam at concentrations of 0, 0.07, 0.5, 1.2, and 5 mg·L^{-1} in 0.01 M CaCl$_2$. All experimental solutions contained 200 mg·L^{-1} Hg(II)Cl$_2$ as a biocide to inhibit biological degradation. To prevent light exposure and photo-degradation, all experimental trials were conducted in screw-capped 8-mL amber vials (or 50-mL Nalgene Oak Ridge Teflon FEP tubes wrapped in aluminum foil). Before starting a trial, soils were preequili-brated in 0.01 M CaCl$_2$. Soil/solution ratios were determined experimentally for each soil and ranged from 1/1 (Willows clay) to 1/50 (Stockton clay adobe), with the goal being to attain experimental soil/solution ratios where the percentage of adsorbed penoxsulam was above 20% and below 80%. The goal of keeping the soil/solution ratios within this range was to permit analysis of changes in aqueous concentrations (both by keeping aqueous concentrations above detection and by ensuring that changes in aqueous concentrations due to soil sorption remain quantifiable) while slurry ratio effects on the soil sorption value were minimized (*16*). In the experiment where the initial solution pH was varied, the same soil/solution ratio of 1:1.33 was used in Willows clay and San Joaquin loam.

After addition of penoxsulam, the soil/buffer slurries were agitated for an appropriate time to achieve equilibrium. All soils were at or near equilibrium after 10 h, as determined in a preliminary experiment. After agitation for a sufficient period to achieve equilibrium, the slurries were separated by centrifugation (5 min at 2500g) and a 1-mL aliquot of the aqueous phase was withdrawn and transferred to an 8-mL liquid scintillation vial containing 7 mL of liquid scintillation (LSC) cocktail. [^{14}C]Penoxsulam concentrations were determined with a TRI-CARB liquid scintillation analyzer Model 2000CA (Packard; Downers Grove, IL). On the basis of the measured radiotracer concentration, the soil adsorption was determined by calculating the difference between the amount of test substance initially present in solution (determined by measuring controls) and the amount remaining at the end of the experiment. Controls consisted of solutions of 12 mg·L^{-1} of unlabeled penoxsulam and 0.03 mg·L^{-1} of [^{14}C]penoxsulam in 0.01 M CaCl$_2$ and 200 mg·L^{-1} Hg(II)Cl$_2$ (no soil). The controls were subjected to precisely

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the same steps as the test systems. There was no evidence for a loss of penoxsulam by adsorption to the tubes or chemical degradation.

The experimental results were fitted to the Freundlich equation

$$c_s = K_F \cdot c_w{}^n \qquad (1)$$

where c_s is the concentration of penoxsulam adsorbed in soil, c_w is the concentration of penoxsulam in solution, K_f is the Freundlich adsorption coefficient, and n is a constant indicating the nonlinearity of the adsorption isotherm (*17*). The soil–water partition constant K_d, the organic matter–water partition constant K_{om}, and the organic-carbon-normalized soil–water partition constant K_{oc} were derived from eq 1 by using eqs 2–4:

$$K_d = K_F \cdot c_w{}^{n-1} \qquad (2)$$

$$K_{om} = \frac{K_d}{f_{om}} \qquad (3)$$

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad (4)$$

RESULTS AND DISCUSSION

Air–Water Partitioning. K_H can either be estimated on the basis of a chemical's vapor pressure (P^0, Pa) and water solubility (S; mol·L^{-1}), or it can be experimentally determined. We attempted to measure K_H with the gas-purge method (*15*) and to examine the effect of temperature on air–water partitioning. However, no changes in the aqueous concentration of penoxsulam were observed in any of the experiments at the maximum feasible flow rate of 1000 mL·min^{-1}. Therefore, it was not possible to obtain an experimental value for K_H. This result indicates that volatilization from water to air is a negligible dissipation pathway for penoxsulam.

This experimental result is confirmed by estimated air–water partition coefficient values for K_H. At 25 °C, K_H was calculated as 8.1×10^{-9} Pa·L·mol^{-1} (pH 5), 1.1×10^{-12} Pa·L·mol^{-1} (pH 7), and 3.1×10^{-11} Pa·L·mol^{-1} (pH 9). The corresponding dimensionless air–water partition constants K_H' are 3.3×10^{-13} (pH 5), 4.6×10^{-15} (pH 7), and 1.3×10^{-15} (pH 9). At 45 °C, K_H was calculated as 8.1×10^{-7} Pa·L·mol^{-1} (pH 5), 1.1×10^{-10} Pa·L·mol^{-1} (pH 7), and 3.1×10^{-9} Pa·L·mol^{-1} (pH 9). The corresponding dimensionless air–water partition coefficients K_H' are 3.3×10^{-11} (pH 5), 4.6×10^{-13} (pH 7), and 1.3×10^{-13} (pH 9). Chemicals with a K_H' of less than 10^{-9} are considered nonvolatile and will remain in the water after application (*18*). This indicates that even under the most favorable conditions for chemical volatilization, i.e., the high temperatures of an extremely hot summer day, penoxsulam would be considered nonvolatile and remains in the water.

Chemical Stability in Water. After turning off the gas and termination of the air–water partitioning experiment, the penoxsulam solution, which included Hg(II)Cl$_2$ as a biocide, was kept in the light-tight and airtight gas purging vessel and maintained at a temperature of 40 °C. Periodically, samples were taken over a period of 3 weeks. There was no measurable decrease in the aqueous concentration over time. The lack of degradation indicates the chemical stability of penoxsulam, at near-neutral pH values, under exclusion of light or organisms.

Soil–Water Partitioning. Soil adsorption isotherms of penoxsulam in four representative rice field soils of the Sacramento Valley are shown in **Figure 2**. K_F values for Willows clay, Sacramento clay, San Joaquin loam, and Stockton
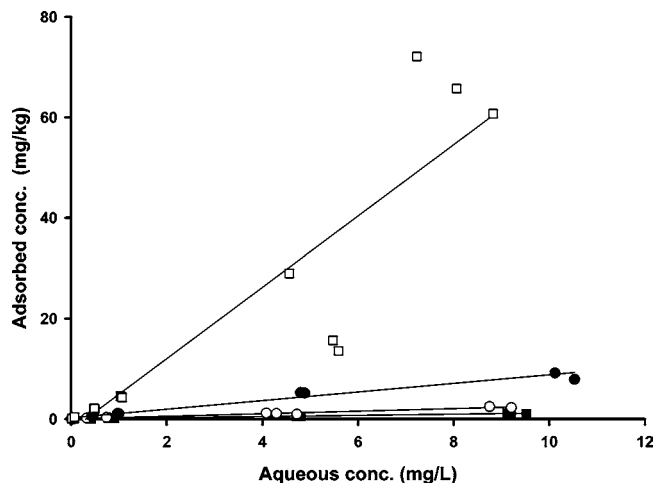

Figure 2. Adsorption of penoxsulam on Sacramento clay (○), San Joaquin loam (●), Stockton clay adobe (□), and Willows clay (■).

Table 2. Soil Sorption Parameters of Penoxsulam in Test Soils[a]

| soil | Freundlich coefficients | | | K_d |
	K_F	n	r^2	
Sacramento clay	0.33	0.90	1.00	0.39
San Joaquin loam	1.10	0.93	1.00	1.21
Stockton clay adobe	5.00	0.99	0.98	5.05
Willows clay	0.13	0.98	1.00	0.14

[a] Freundlich coefficients were obtained by fitting the experimental results to eq 1 by linear regression analysis (*6*). K_d was calculated from the determined Freundlich coefficients by using eq 2.

clay adobe were 0.13, 0.33, 1.10, and 5.00, respectively. In all cases, n was close to 1 (**Table 2**), indicating that the Freundlich adsorption isotherms (see eq 1) can also be approximated with linear isotherms:

$$K_d \approx K_F \qquad (5)$$

The results indicate that initial aqueous concentrations of less than 12 mg·L^{-1} did not saturate potential sorption sites of the soils. The recommended application rate of 40 g·ai/ha (*2*) yields field water concentrations well below this value.

There was no significant relationship between the organic carbon and organic matter contents and K_d values. Instead, there was a strong inverse relationship between the soil pH and K_d (**Table 2** and **Figure 3**). The soil sorption values (K_d) were smallest in the neutral soils, Willows clay (pH 6.8) and Sacramento clay (pH 6.5), with mean values of 0.14 and 0.39. K_d values <1 indicate that penoxsulam is qualitatively mobile, and there is no significant retention in soil (*6*). In comparison, sorption was increased but still low in the acidic soils, San Joaquin loam (pH 5.3) and Stockton clay adobe (pH 4.6), with mean K_d values of 1.21 and 5.05.

Influence of pH on Adsorption. The mean K_d values of the four soils (**Table 2**) showed a strong relationship with soil pH:

$$\log K_d = -0.64(\text{soil pH}) + 3.61 \quad (r^2 = 0.97) \qquad (6)$$

Therefore, the soil pH could potentially be used as an indicator to predict the adsorption capacity of a particular soil for penoxsulam. The effect of the initial solution pH on K_d was negligible, due to the pH buffering capacity of the soils. In San
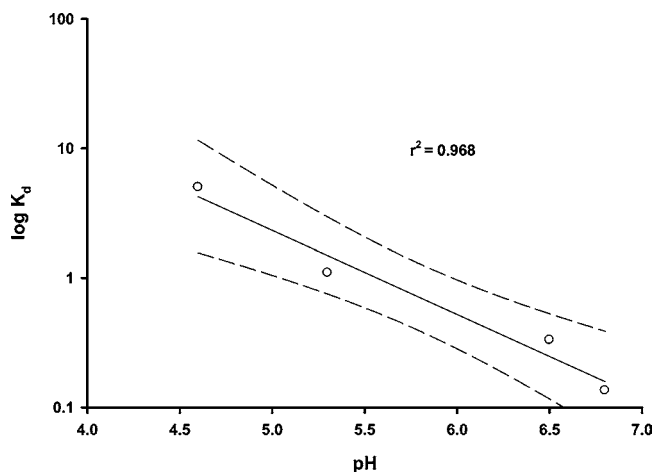
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Figure 3. Effect of the soil pH on the adsorption coefficient of penoxsulam in Sacramento Valley rice soils.
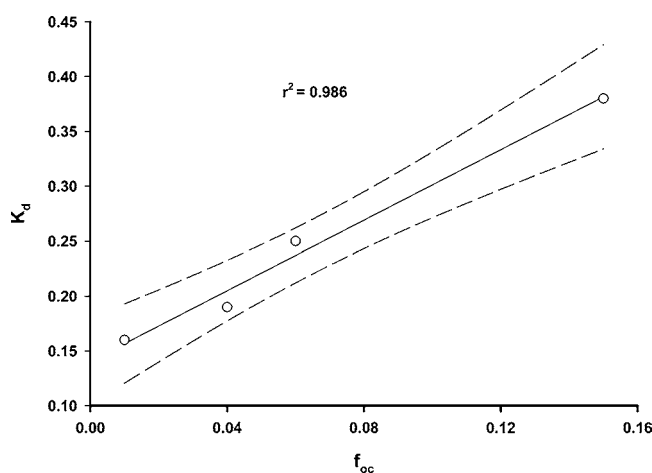

Figure 4. Effect of manure compost amendments on the soil sorption value of penoxsulam in Willows clay.

Joaquin loam, K_d exhibited a weak relationship with the initial solution pH ($r^2 = 0.43$). The mean sorption values at the lowest pH (pH 3) and the highest solution pH (pH 9) were slightly but significantly different ($p = 0.014$) with K_d (pH 3) = 0.453 ± 0.003 ($n = 3$) and K_d (pH 9) = 0.433 ± 0.003. In Willows clay, the solution pH did not have a significant effect on the sorption value. A plausible explanation is that Willows clay has a higher pH buffering capacity than San Joaquin loam, as indicated by its higher CEC value (see **Table 1**).

The pH-dependency of soil sorption values for penoxsulam is in agreement with the pH-dependency of its water solubility (*1*). At near-neutral pHs, penoxsulam is thought to exist almost exclusively as an anionic species, presumably due to the deprotonation of its sulfonylamido group (*19*) (see **Figure 1**). At lower pH values, the ratio of the anionic to the neutral species would shift toward the latter, which is presumably less soluble and less mobile in soil (*16*).

Influence of Organic Matter on Adsorption. In Willows clay amended with different levels of manure compost, there was a strong linear relationship between the K_d and the soil organic carbon content ($r^2 = 0.999$; **Figure 4**). However, the correlation of mean K_d for samples amended with the largest fraction of organic matter ($f_{oc} = 0.15$) was still low at 0.38. Stripping the soils of organic matter by H_2O_2 treatment reduced the K_d by a factor of 0.32. The results indicate that sorption of penoxsulam occurs to both organic matter and clay mineral sorption sites.

Conclusions. Penoxsulam is scheduled for application in California rice fields by 2005. To develop best management practices, partition data need to be widely available that permit an assessment of the distribution of penoxsulam between air, water, and soil. The measured K_d and K_F values in representative California rice soils suggest that penoxsulam is highly mobile in soil but will not evaporate from water into the ambient air. Hence, dissipation rates of penoxsulam are expected to be controlled by biological and photochemical processes and by offsite transport in water.

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