Dissipation of Penoxsulam, a New Sulfonamide Herbicide, in Simulated Rice Field Conditions

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Abstract

Penoxsulam (trade name Granite) is a new acetolactate synthase (ALS) inhibitor herbicide for post-emergence control of annual grasses, sedges, and broadleaf weeds in rice culture. This laboratory study ascertains microbial and photochemical degradation rates and transformation pathways as well as partition constants under conditions simulating California flooded rice field conditions. Soil sorption values were inversely related with the pH and ranged from 0.14 to 5.3, indicating that penoxsulam is qualitatively mobile and there is no significant retention in the soil. Penoxsulam did not partition into air at any measurable rate at 20°C or 40°C and its K_H (pH 7) was estimated at 4.6 x 10-15 Pa · L · mol-1 based on available water solubility and vapor pressure data.. Biodegradation studies in microcosms simulating flooded conditions reveal a DT50 of 6-21 d. No residual metabolites where detected. Photodegradation was also examined under natural irradiation and revealed half-lives of 3-9 d. Seven photoproducts were identified. Results imply that dissipation of penoxsulam in flooded rice fields is rapid and controlled by microbial and photochemical degradation rates.

Introduction

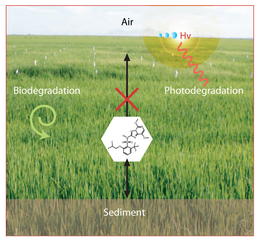
Penoxsulam (Tradename Granite, Dow AgroSciences LLC) is a triazolopyrimidine sulfonamide that works as an ALS (acetolactate synthase) inhibitor and is intended for control of grass, broadleaf, and sedge weeds in rice (1). Penoxsulam is not expected to pose a threat to aquatic or terrestrial animals or humans, but there is a possibility that it may harm special status plants and aquatic foodweb organisms if not appropriately managed (2).

Purpose of Study

- Determine partition constants (air/water, soil/water) and degradation rates (photo- and biodegradation) to assess the relative persistence of penoxsulam in rice fields and their tailwaters.
- Determine the formation and persistence of degradation products.
- Establish degradation pathways.

Objectives

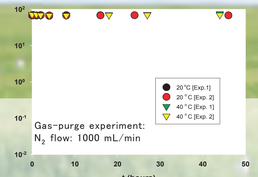
- **Partitioning:** Determine soil sorption values for California rice soils and Henry's air/water constant.
- **Degradation:** Determine rates and products for biodegradation and photodegradation.



Results

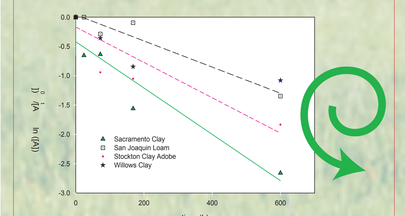
Air-Water Partioning

- Extremely low vapor pressure: 9.5 x 10-14 Pa at 25ºC
- Calculated $K_H = P_0/S = 1.1 \times 10\text{-}12$ Pa · L · mol –1
- Chemicals with $K_H < 3 \times 10\text{-}5$ Pa · L · mol –1 are non-volatile

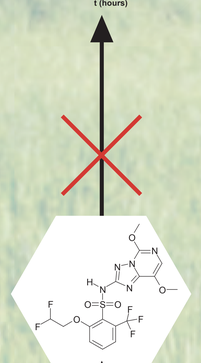


Biodegradation

- Approximate half-live in flooded rice field soils: 6-21 days
- Penoxsulam will be rapidly biodegraded in flooded rice soils



	$t_{1/2}$ (d)	k_p (h^{-1})	RSD (%)	r^2
Sacramento clay	7.2	0.0040	20.0	0.8957
San Joaquin loam	13.1	0.0022	13.6	0.9313
Stockton clay adobe	9.6	0.0030	36.6	0.7182
Willows clay	16	0.0018	33.3	0.7392

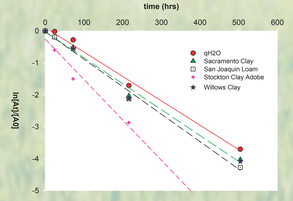


Hv

Photodegradation

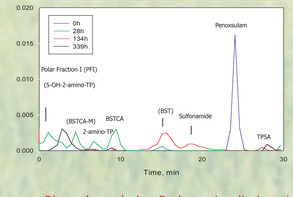
Photolysis rates in sunlight

- Approximate half-live in rice field waters: 3-9 days; pH-dependent
- Penoxsulam will be rapidly photodegraded in rice fields

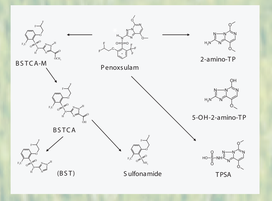


Water origin	$t_{1/2}$ (d)	k_p (h^{-1})	RSD (%)	r^2	△q-H2
q-H_2O	8.3	0.0167	5.3	0.9958	
Sacramento clay	7.9	0.0178	4.9	0.9959	
San Joaquin loam	7.4	0.0189	4.7	0.9967	*
Stockton clay adobe	5.0	0.0277	15.1	0.9822	*
Willows clay	7.8	0.0180	7.3	0.9951	

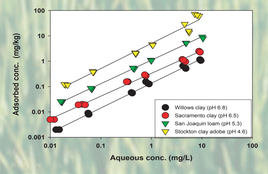
Photodegradation in "merry-go-round" reactor (3000 Å)



Photodegradation Pathway (preliminary)



Sediment



- K_F <1 : penoxsulam is qualitatively mobile
- Sorption value is correlated with soil pH (r^2 = 0.97)
- no correlation with soil organic carbon

	pH	% OC	K_F	n	r^2
Willows clay	6.8	1.12	0.13	0.98	1.00
Sacramento clay	6.5	1.33	0.33	0.90	0.98
San Joaquin loam	5.3	0.50	1.10	0.93	1.00
Stockton clay adobe	4.6	0.74	5.00	0.99	1.00

Materials & Methods

Standards

Technical grade penoxsulam and nine transformation products as well as 14C (-14C-TP & -Ph-UL-14C) and 13C isotopes were generously provided by Dow AgroSciences LLC.

Henry's Air-Water Partition Constant K_H

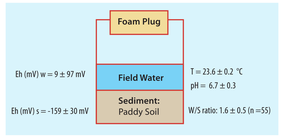
1. Bubble Chamber Method (4)
2. Calculated from vapor pressure and solubility

Soil Sorption Values by Batch Equilibrium Method (4)

- Added solutions of 0.03 mg/L [14C]penoxsulam and ranging concentrations of "cold" penoxsulam to soil/buffer slurries
- At equilibrium: $C_{water} = MW*(100\text{-}\%adsorbed\ 14C)*C_{water(t=0)}$
- Freundlich isotherm fit: $C_L = K_F \times C_w^n$

Biodegradation in Rice Paddy Incubation Conditions (5,6)

- Flooded (anaerobic) soils in open, aerated systems:



- Acclimate for 7-14 days before adding penoxsulam at ~ 6 ug/mL (max. application rate)

Photodegradation

Approximate rate constant in outdoor experiment using aqueous solutions in 10-mL borosilicate tubes with Teflon-lined caps.

Extraction

- **Water:** HLB SPE; elute with ACN:MeOH:AcOOH (50:50:1)
- **Sediment:** shake & extract 2x1h with ACN, rotovap, reconstitute in 0.1 M HCl, then same as water phase
- **Surrogate spiking standard:** cloransulam-methyl
- Penoxsulam Q1/Q3 484/195

LC-MS /MS (HILIC)

- Electrospray ionization
- **Column:** Polaris Si 3u/50 x 4.6 mm
- Injection Volume: 10 uL
- Flow rate: 750 uL/min (150 uL/min split to source)
- Gradient (positive): ACN:1%AcOOH 0 min (75:25), 1 min (75:25), 2 min (40:60), 2.1 min (75:25), 5 min (75:25)
- Gradient (negative): MeOH:H2O (50mM NH4acetate): 0 min (100:0), 1 min (28:72), 3.1 min (100:0), 6 min (100:0)
- Internal Standard: 13C-Isotope

Photodegradation Pathway (preliminary)

HPLC/C14 Co-Chromatography

- Column: RP Inertsil ODS C-18 5u/250 x 4.6 mm
- Injection Volume: 20 uL
- Flow rate: 1000 uL/min

	H2O (0.01% ACOOH)	ACN
Time	85	15
0 min	60	40
10 min	30	70
20 min	85	15
23 min	85	15
35 min	95	5

Discussion

Our results indicate that penoxsulam is qualitatively mobile in soil and does not volatilize into the ambient air. The environmental fate of penoxsulam in rice fields is expected to be controlled by photo- and biodegradation kinetics. With photolysis half-lives ranging between 3 and 9 days, and biological degradation half-lives between 6 and 21 days, it is expected to be non-persistent in the rice field environment and tailwaters. Photodegradation studies in natural and simulated solar radiation indicated the presence of transformation products with considerably slower photodegradation rates. However, these products could not be detected in field samples. The 2-ATP metabolite was found to be rapidly biodegradable in microcosm studies, with a half-live of 1.25 days (results not shown here).

Key Findings

Penoxsulam

- is qualitatively mobile in soil.
- does not volatilize.
- is expected to dissipate rapidly due to both photo- and biodegradation.
- yields no residual breakdown products.

Conclusions

- Based on this study and best management practices assumed, no particular management advisories for penoxsulam.
- Establishing a more complete fate and ecotoxicology profile is recommended for exposure modeling and risk assessments, e.g. special status plants, aquatic foodweb organisms in receiving waters.

FOR MORE INFORMATION PLEASE CONTACT *thomasj@sfei.org*

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