Data Evaluation Report on the aquatic field dissipation of penoxsulam

PMRA Submission Number {......} EPA MRID Number 46703503

Data Requirement: PMRA Data Code:
EPA DP Barcode: D325783
OECD Data Point:
EPA Guideline: 164-2

Test material: Penoxsulam

End Use Product name: GF-443 SC SF **Concentration of a.i.:** 21.4%
Formulation type: Aqueous suspension concentrate

Test material:

Common name:	Penoxsulam.
Chemical name:	
IUPAC name:	3-(2,2-Difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-α,α,α-trifluorotoluene-sulfonamide. 2-(2,2-Difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide. 6-(2,2-Difluoroethoxy)-N-(5,8-dimethoxy-s-triazolo[1,5-c]pyrimidin-2-yl)-α,α,α-trifluoro-o-toluenesulfonamide.
CAS name:	2-(2,2-Difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide.
CAS No.:	219714-96-2.
Synonyms:	XDE-638; DE-638; TSN101649; SP1019 (SePRO).
Smiles string:	FC(c1cccc(c1S(=O)(=O)N(c1nn2c(n1)ccnc2))OCC(F)F)(F)F (ISIS v2.3/Universal SMILES). No EPI Suite, v3.12 SMILES String found as of 6/27/06. n1c(nc2n1c(ncc2OC)OC)NS(=O)(=O)c3c(cccc3C(F)(F)F)OCC(F)F.

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Company Code
Active Code
Use Site Category
EPA PC Code: 119031

CITATION: Newcombe, A.C., J.A. Knuteson and D.G. Petty. 2005. Penoxsulam aquatic dissipation following multiple treatments to a Florida lake. Unpublished study performed by LFR Levine-Fricke, Tallahassee, FL; Pyxant Laboratories, Inc., Colorado Springs, CO; and Agvise Laboratories, Inc., Northwood, ND; and submitted by SePRO Corporation, Carmel, IN (p.16). Laboratory Study ID: LK-2004-01. Experiment initiation April 4, 2004 and completion March 29, 2005 (p.3). Final report issued November 1, 2005.

EXECUTIVE SUMMARY

Penoxsulam (3-(2,2-difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-*c*]pyrimidin-2-yl)-α,α,α-trifluorotoluene-2-sulfonamide; GF-443 SC SF, 21.4% a.i.) was applied four times, at approximately 28-day intervals by subsurface injection, to a 1.2-ha application zone of an approximately 12.2-ha lake in Florida. Each application was made to achieve a whole-lake water concentration of approximately 20 μg penoxsulam/L. The maximum proposed single use rate was reported as 150 μg penoxsulam/L. The fourth application was made concurrently with the conservative tracer Rhodamine WT dye to determine the three-dimensional dispersal pattern in the lake water. Water and sediment samples were collected for analysis of penoxsulam only. Composite water samples were collected within 1.5-6 hours following each application in an attempt to estimate the penoxsulam application rate. Water samples (both mid-depth in the water column and 25 cm from lake bottom) were then collected from nine sampling locations at approximately 1, 3, 7, 10, 20, and 27 days after the first three applications, and at 1, 3, 7, 11, 21, 28, 43, 55, 83, 109, 137, 167, and 210 days after the fourth application. Samples were also collected from three additional sampling stations installed prior to the fourth application, within the emergent vegetation zone of the lake. Sediment samples were collected at the same sampling intervals for water. All samples were analyzed within 349 days of collection.

The Rhodamine WT dye dispersion analysis results indicated that Rhodamine dye had become widely dispersed throughout the lake by 6 hours posttreatment, and that complete lateral and vertical mixing was achieved by approximately 1 day posttreatment.

Penoxsulam dissipated in the water with calculated half-lives of 15.4 days ($r^2 = 0.9849$), 11.0 days ($r^2 = 0.9957$), 12.1 days ($r^2 = 0.9786$), and 11.7 days ($r^2 = 0.9928$) following each of the four applications, respectively, calculated using linear regression analysis performed on a plot of ln-transformed penoxsulam concentrations vs. time and the equation $t_{½} = -ln\ 2 / k$, where k is the rate constant.

The mean measured penoxsulam concentration in water was initially 23.15-34.25 ng/mL at 0-1 days following each of the first three applications, and decreased to 5.35-8.30 ng/mL by 27-28

days posttreatment (0-1 days prior to the subsequent application). Following the fourth application, penoxsulam was detected at a mean concentration of 26.27-27.47 ng/mL from 0 to 3 days, decreased to 13.13 ng/mL by 11 days, 4.99 ng/mL by 28 days, 0.85 ng/mL by 55 days, and was last detected at 0.01 ng/mL at 137 days posttreatment. Results showed that spatial distribution was accomplished by 3 days after each application. Mean penoxsulam concentrations at 3 days posttreatment ranged from 19.85 to 26.39 ng/mL or 99.3-132% of the target lake concentration. Vertical mixing was accomplished by 1-3 days posttreatment. Mean concentrations of penoxsulam residues in water are presented in the table below.

Penoxsulam concentrations in water, expressed as ng/mL.

Days posttreatment	Average concentration (ng/mL)	Range (mid water column depth)	Range (25 cm above sediment)
Application 1			
0	28.71	4.17-78.9	3.97-45.2
1	29.14	18.0-41.0	15.8-45.5
3	26.28	25.6-33.7	22.1-26.0
7	21.83	20.1-23.6	20.7-22.9
10	20.67	19.1-22.7	18.1-23.2
20	13.26	11.8-13.8	12.0-14.3
27	8.30	7.64-9.13	6.92-8.92
Application 2			
0	34.25	8.02-126	8.59-45.6
1	29.80	24.6-35.0	21.4-38.9
3	25.59	24.3-27.8	22.6-26.7
7	19.79	19.2-20.5	19.4-20.4
10	16.96	16.3-17.2	16.6-17.5
20	9.63	8.98-9.67	4.86-18.5
28	5.35	5.23-5.60	4.94-5.52
Application 3			
0	24.63	12.8-44.6	7.33-35.9
1	23.15	20.2-29.6	19.1-26.3
3	19.85	19.4-20.8	16.3-20.8
7	17.29	16.4-19.2	14.8-18.6
11	14.90	12.3-17.6	13.6-16.9
20	6.77	4.88-13.4	6.27-6.91
27	5.58	4.57-10.6	4.38-5.92
Application 4			
0	26.27	3.76-104	4.15-46.0
1	27.47	2.32-36.1	21.7-35.7
3	26.39	11.3-34.3	19.4-28.7
7	16.73	3.15-18.6	14.4-19.7
11	13.13	7.40-14.6	9.04-14.6
21	8.38	6.02-8.76	7.90-8.66
28	4.99	1.88-5.15	4.62-5.12
43	1.33	0.796-1.46	1.06-1.74
55	0.85	0.665-0.963	0.614-1.02
83	0.12	0.0879-0.179	0.0731-0.153
109	0.05	0.0500-0.0607	0.0479-0.0580
137	0.01	ND-0.0212	ND-0.0255

167	ND	ND	ND
210	ND	ND	ND-0.0176

Penoxsulam dissipated in the sediment with calculated half-lives of 8.2 days ($r^2 = 0.9046$), 12.9 days ($r^2 = 0.7256$), 7.8 days ($r^2 = 0.7225$), and 21.7 days ($r^2 = 0.7019$) following the four applications, respectively, calculated using linear regression analysis performed on a plot of ln-transformed penoxsulam concentrations vs. time and the equation $t_{½} = -ln\ 2 / k$, where k is the rate constant.

Penoxsulam concentrations in sediment mirrored those seen in the water. The mean measured penoxsulam concentration in sediment was initially 10.86 ng/g at 1 day following the first application and decreased to 0.80 ng/g by 27 days posttreatment, was initially 2.94 ng/g immediately following the second application, and decreased to 0.81 ng/g by 28 days posttreatment, and was initially 6.96 ng/g immediately following the third application and decreased to 0.51 ng/g by 27 days posttreatment. Following the fourth application, penoxsulam was detected at a mean concentration of 2.13 ng/g at 1 day, was a maximum of 3.75 ng/g at 3 days, then decreased to 1.53 ng/g by 21 days, and was last detected above the LOD at 1.18 ng/g at 28 days.

Penoxsulam concentrations in sediment, expressed as ng/g.

Days posttreatment	Average concentration (ng/g)	Range (ng/g)
Application 1		
1	10.86	3.14-29.9
3	3.82	1.84-5.51
7	4.09	1.36-12.9
10	3.57	2.16-6.22
20	1.46	ND-2.78
27	0.80	ND-2.87
Application 2		
1	2.94	1.42-9.89
3	5.02	ND-13.2
7	3.08	1.95-4.14
10	4.51	2.41-6.15
20	2.11	ND-4.83
28	0.81	ND-3.01
Application 3		
1	6.96	ND-16.7
3	4.55	1.65-10.5
7	0.85	ND-1.97
11	2.28	ND-8.81
20	0.74	ND-2.54
27	0.51	ND-2.09
Application 4		
1	2.13	ND-3.73
3	3.75	ND-8.41
7	2.26	ND-5.97
11	2.60	1.57-7.31
21	1.53	ND-2.82

28	1.18	ND-3.13
43	ND	ND
55	ND	ND
83	ND	ND
109	ND	ND
137	ND	ND
167	ND	ND
210	ND	ND

Total rainfall during the 9.5-month study period was 136.43 cm or 127% of the pro-rated annual historical rainfall total. The authors stated that water quality parameters (pH range of approximately 6-8; dissolved oxygen range of 0.6-13.5 mg/L; conductivity range of 0.03 to 0.05 mS/cm) were typical of Florida lakes and that visibility readings indicated that the lake moved from a eutrophic state to a hypereutrophic state during the course of the study.

Study Acceptability: This study is classified as supplemental. Transformation products were not monitored. The target application rate was 13% of the maximum single use rate. No significant deviations from good scientific practices were noted.

MATERIALS AND METHODS

The aquatic field dissipation of penoxsulam (GF-443 SC SF, 21.4% a.i.; water solubility = 0.408 g/L in pH 7 buffer at 19°C; vapor pressure = 2.49×10^{-14} Pa at 20°C; p.21; Table 1, p.86) was studied using an approximate 12.2-ha lake located in Madison County, Florida, approximately 9 kilometers west-southwest of the town of Madison (30.430633 N latitude, 83.500783 W longitude; pp.22-24; Table 3, p.88; Figure 2, p.161). The lake selected had no outflow and no significant inflow channels. A floating island of approximately 0.5 ha and consisting of matted vegetation and small trees was secured in place prior to application. The maximum water depth of the lake was approximately 1.8 m (p.52). A bathymetric survey and a shoreline elevation survey were conducted as part of the site characterization (pp.52-53; Figure 5, p.164). Results indicated a mean water column depth of 3.4 ft; the survey also revealed the presence of an unconsolidated flocculent sediment layer at the lake bottom that varied in thickness from 20 to 36 cm. Three water and sediment samples were collected for characterization 2 days prior to the first test application (pp.26-27). Mean results were as follows for lake water: pH 7.6, hardness 30 mg $CaCO_3$/L, conductivity 0.08 mmhos/cm, total dissolved solids 21 ppm, turbidity 3.49 NTU, alkalinity 13 mg $CaCO_3$/L (Table 14, p.120). The sediment was classified as a sandy clay loam (47.7% sand, 22.0% silt, 30.3% clay, pH 4.6, 24.4% organic carbon, CEC 58.2 meq/100 g, bulk density 0.56 g/cm^3; Table 15, p.121). A three-year plot history was not provided for the test site. However, there was no documented history of penoxsulam in the lake or on the adjacent land (p.23). An on-site meteorological station was installed on the north side of the lake to measure rainfall, air temperature, relative humidity, wind speed and direction, and solar radiation (p.28). Additionally, a thermocouple stack was installed in the 1.2-ha application zone of the lake at sampling station A (Figure 1, p.160) to measure the water temperature profile and surface sediment temperature, and a water quality meter was installed at approximately mid-depth in the water column (90 cm from bottom sediment) at sampling station A to record dissolved oxygen, temperature, pH and electrical conductivity (pp.29-30). Other instrumentation installed at sampling station A included a water depth gauge to measure fluctuations in the water depth. Also, visible light penetration and UV-B light penetration were measured at each sampling event (p.31). Visible light penetration was measured using a standard 20-cm diameter Secchi disk. UV-B light penetration was measured using a Skye Instruments UV-B light sensor and a portable hand-held SpectroSense meter. Light penetration measurements were initially made from sampling station A, but were relocated to between sampling stations C and D on the eastern side of the lake during the study because the depth of the water column was lower and did not allow light penetration to the sediment.

Prior to test application, nine water and sediment sampling stations were positioned around the lake (p.32). Three sampling stations were positioned within the 1.2-ha application zone located in the center of the lake (stations A, H, and I), and the other six stations (B, C, D, E, F, and G) were located at distances varying from 175-294 ft from the application zone (Figure 1, p.160). All nine sampling stations were positioned where the depth of the water column to the bottom sediment was approximately 120 cm (4 ft). Three additional sampling stations (J, K, and L) were established prior to the fourth penoxsulam application on the northern end of the lake (10-100 cm water depth) within the emergent vegetation zone.

Penoxsulam was applied by subsurface injection to the center 1.2-ha application zone (122.8 x 98.8 m rectangular zone; p.37) of the lake on April 7, May 5, June 3, and July 1, 2004 (approximately 28-day intervals; pp.33-34). The first application was made to achieve a whole-lake water concentration of approximately 20 µg penoxsulam/L. Subsequent applications were made at 16.1, 15, and 16 µg penoxsulam/L, and were targeted to return the whole-lake concentration to a nominal 20 µg penoxsulam/L. The application was made from a 4.3-m long fiberglass hulled Carolina skiff boat using three 1.8-m length rubber hoses equipped with a single Disc #12 spray nozzle and connected to a 1.8-m manifold boom. The hose arrangement provided an effective application-path width of 2.74 m. Each of the four test applications required the preparation of six tank mixes (p.35). Only water obtained from the test site was used to prepare the tank mixes. For the first three applications, a spray volume of 50 gal was prepared and for the five subsequent tank mixes, a spray volume of 41 gal was prepared (p.36; Table 7, p.92); no tank mix adjuvants or antifoam agents were used for the first three application tank mixes. A total of 36 application passes were needed for each application (p.37; Figure 4, p.163). Application pass times and sprayer output following each pass were reported in Table 9 (pp.94-95), and indicate the uniform output of spray solution and close adherence to the target output (pp.37-38).

The fourth penoxsulam application was made concurrently with the conservative tracer Rhodamine WT dye (21.3% a.i.; Table 2, p.87) to determine the three-dimensional dispersal pattern in the lake water (pp.25 and 34). Compatibility experiments conducted prior to the test application indicated that the dye could be safely mixed with the penoxsulam test formulation with no adverse impact (p.25). The dye was applied to achieve a nominal whole-lake concentration dye concentration of approximately 6 µg/L (p.34). De-Foamer antifoam agent was also added to each of the six spray tanks comprising the fourth application (p.36). A total of 37 dye sampling stations were located in the open water of the lake to monitor the dye dispersion in real time (Figure 3, p.162).

Tank mix samples were collected in duplicate just prior to application and just before the spray volume was exhausted for each tank mix for the first three test applications, and in triplicate for the fourth application tank mixes (pp.39-40). Tank mix samples were mixed with approximately 75 mL of tetrahydrofuran (THF) and extracted by shaking by hand (p.48). Samples were analyzed for penoxsulam by LC with UV detection (operating conditions reported in Appendix E, Figure 8, p.577). Samples were analyzed within 36 days of collection (p.50). Calculated recoveries of penoxsulam in the tank mix were 102%, 97.5%, 95.5%, and 107% of the theoretical for the first through fourth applications, respectively (Table 21, pp.128-129; based on the registrant-calculated theoretical values reported in p.63).

Meteorological conditions during the applications were as follows: Application 1: maximum air temperature 25.14°C, maximum relative humidity 71.40%, maximum wind speed: 5.13 m/s, cloud cover 50%; Application 2: maximum air temperature 26.27°C, maximum relative humidity 63.37%, maximum wind speed: 3.73 m/s, cloud cover 0%; Application 3: maximum air temperature 30.89°C, maximum relative humidity 81.20%, maximum wind speed: 4.25 m/s, cloud cover 10%; Application 4: maximum air temperature 32.02°C, maximum relative humidity 83.90%, maximum wind speed: 2.98 m/s, cloud cover not reported (Table 5, p.90).

Verification of the application rate was not possible due to the subsurface application method. However, composite water samples were collected between approximately 1.5 and 6 hours following each test application (pp.41-42). Composite water samples were collected along six sampling transect lines that extended the entire length of the application zone and ran perpendicular to the direction of the application passes. Samples were collected from a 3-m Jon boat traveling at constant speed across the application zone and using a peristaltic pump to draw water at a constant flow rate into a 1-L Mason jar. Samples were collected via two lengths of HDPE sample collection tubing attached to a 5-cm PVC guide rod. One tube collected water at approximately 25 cm from the lake bottom, and the other collected water from approximately mid-depth of the water column. Following collection, a portion of the water collected into the Mason jar was transferred to two sampling vials (20 mL of sample in 40-mL vials), and the rest was poured back into the application zone.

Water samples were collected prior to treatment and at approximately 1, 3, 7, 10, 20, and 27 days after the first three applications, and at 1, 3, 7, 11, 21, 28, 43, 55, 83, 109, 137, 167, and 210 days after the fourth application (Tables 10, p.96). At each sampling interval, duplicate samples (20 mL) were collected from approximately mid depth in the water column, and 25 cm from the lake bottom from sampling stations A through I using a Wheaton type grab sampler (p.40; Figure 1, p.160). Samples collected from stations J, K, and L in the emergent zone were collected by hand from mid-depth only. Samples were placed into an on-site freezer. Samples were analyzed within 339 days of collection (p.50).

Sediment samples were collected at the same sampling intervals for water except that sediment was not sampled on the day of the test applications (Tables 10 and 26, pp.96 and 158, respectively). Sediment samples were collected within a 3-m radius of sampling stations A through G using a sediment dredge sampler (p.42; Figure 1, p.160). Following collection, the sediment was cleaned of any plant detritus, and a 100-g aliquot was transferred to a metal sample container and the rest was discarded back into the lake outside of the 3-m radius collection area. Samples were placed into an on-site freezer. Samples were analyzed within 349 days of collection (p.50).

Water samples were collected for real-time Rhodamine WT dye dispersion analysis at 0, 2, 6, 21, 27, and 75 hours posttreatment of the fourth application from the 37 designated sampling stations (p.53; Figure 3, p.162; Table 12, pp.98-109). Samples were collected from a small boat using a small bilge pump with an attached garden hose; analysis was performed using an analog fluorometer equipped with a flow-through cell (pp.43-44). Samples were collected at the mid-depth and at the bottom of the water column. Sampling from all stations required approximately 1.5 hours (p.53). Additional samples were collected for laboratory Rhodamine WT dye analysis at 1 day prior to the fourth application and at 0, 1, 3, 7, 11, 21, and 28 days posttreatment (p.44; Table 10, p.96). Samples were collected from sampling stations A through L at day 0 and 1 day posttreatment, and from stations A, B, C, D, E, F, G, J, K, and L at all subsequent sampling intervals. Samples were collected from approximately 25 cm from the bottom sediment and at mid-depth in the water column and were collected in the same manner as the samples collected for penoxsulam residue analysis. Sample aliquots (1 mL) were analyzed by a bench top hand-held fluorometer (p.48). A solid Rhodamine WT standard (approximate concentration 32 ppb) was included in each sample set analyzed. The manufacturer quoted LOD was 0.4 µg/mL (p.50).

Water and sediment samples were analyzed for penoxsulam only (pp.45-47).

Penoxsulam in water was analyzed by DAS method GRM 02.15 with minor modifications until penoxsulam residues decreased to below the LOQ of the method, and were then analyzed by DAS method GRM 01.30 with minor modifications (pp.45-46; Appendix E, pp.459-462 and Figure 3, p.573). For DAS Method 02.15, samples were thawed in the dark and a 1-mL aliquot was analyzed for penoxsulam by HPLC (Varian Metasil AQ C18 column, 5 µm, 50 x 2 mm; mobile phase of 1 mM ammonium acetate in water:1 mM ammonium acetate in methanol; 50:50, v:v; Appendix E, Figure 5, p.575) with tandem mass spectrometry; the retention time of penoxsulam was 0.85 min. The LOQ was 3.0 ng/mL and the LOD was 0.05 ng/mL. For DAS Method 01.30, samples were thawed in the dark and a 10-mL aliquot was purified by solid phase extraction (Waters Oasis® MAX 3 cartridge). The eluate was evaporated to dryness, reconstituted in 1 mL of acetonitrile:methanol:water:acetic acid (15:15:70:0.1), and analyzed for penoxsulam by LC-MS-MS (Zorbax SB C8 column, 3.5 m, 4.6 x 75 mm; mobile phase of A: water with 0.1% acetic acid and B: methanol:acetonitrile (1:1), A:B, 70:30 to 5:95 to 70:30, v:v; Appendix E, Figure 6, p.576); the retention time of penoxsulam was 5.30 min. The LOQ was 0.05 ng/mL and the LOD was 0.01 ng/mL.

Sediment samples were analyzed by DAS method GRM 01.31 with minor modifications (pp.46-47; Appendix E, pp.462-464 and Figure 4, p.574). After thawing overnight, the samples were mixed with a spatula and approximately 5-g aliquots were extracted by shaking with 25 mL of acetonitrile:hydrochloric acid (1N) in water (90:10, v:v) for 60 minutes. After the supernatant was decanted, the pellet was resuspended in 15 mL of the extraction solution and extracted by shaking for 30 minutes. The combined extracts were brought to volume with the extraction solution and neutralized to a pH between 7 and 8 with concentrated ammonium hydroxide. Aliquots (4 mL) were then evaporated to near dryness, reconstituted in 4 mL of 0.1N hydrochloric acid, and vortexed. Following sonication for 30 seconds, the sample was purified by solid phase extraction (Waters Oasis® HLB cartridge). The eluate was concentrated with a TurboVap LV evaporator at 40°C, reconstituted with 1 mL of 0.1% acetic acid in methanol:acetonitrile:water (5:5:90, v:v:v), and analyzed for penoxsulam by LC-MS-MS as previously described for the water method GRM 02.15 (Appendix E, Figure 7, p.577). The LOQ was 3.0 ng/g and the LOD was 0.05 ng/g.

The efficiency of the analytical methods was determined by fortifying control water and sediment samples collected from the lake pretreatment with penoxsulam at the LOQ and five times the LOQ (pp.39 and 62). Mean recovery of penoxsulam from lake water was 94.1 ± 11.1% for DAS method GRM 02.15 (fortifications at 3.0 and 15.0 ng/mL), and 101.1 ± 13.5% for DAS method GRM 01.30 (fortifications at 0.050 and 0.250 ng/mL), and mean recovery from sediment was 75.2 ± 8.0% (fortifications at approximately 3 and 15 ppb; Appendix E, Tables 3-5, pp.520-530). Results were similar across all fortification levels.

Separate storage stability studies were conducted for penoxsulam in water (MRID 46433901) and soil (MRID 46433902). In brief, in <u>MRID 46433901</u>, 25-mL aliquots of water samples acquired from a California study site were fortified with penoxsulam at 0.03 mg/L and stored refrigerated for up to 433 days and separate samples were stored frozen for up to 320 days. In <u>MRID 46433902</u>, 5-g aliquots of soil samples (from California) were fortified with penoxsulam at 0.03 µg/g and stored frozen for up to 781 days.

In addition, a storage stability study was conducted using water samples collected at 7 days after the fourth test application (p.50). Twenty samples were collected from mid depth of the water column from sampling stations A and H, and two samples were analyzed by DAS method GRM 02.15 following 75, 76, 82, 84, 99, 129, 159, and 190 days of storage.

RESULTS AND DISCUSSION

Penoxsulam (GF-443 SC SF, 21.4% a.i.) was applied four times (approximate 28-day intervals) by subsurface injection to achieve a whole-lake water concentration of approximately 20 µg penoxsulam/L (which is 13.3% of the reported maximum proposed single use rate) to a 1.2-ha application zone of an approximately 12.2-ha lake in Florida.

Results from the real-time Rhodamine WT dye dispersion analysis indicated that Rhodamine dye had become widely dispersed throughout the lake by 6 hours posttreatment (although a vertical gradient was noted) and that similar concentrations were observed at the 37 sampling stations by 21 hours posttreatment (average water column dye concentration of 6.70 µg/L; p.53; Table 12, pp.98-109). Rhodamine dye concentration contour maps showing lateral dye dispersion over time are presented in Figures 7-12 (pp.166-171). Results from the laboratory dye determinations confirmed the real-time dye monitoring data, with the 1-day posttreatment samples indicating that lateral and vertical mixing was achieved (p.54; Table 13, pp.110-119).

Penoxsulam dissipated in the water with calculated half-lives of 15.4 days ($r^2 = 0.9849$), 11.0 days ($r^2 = 0.9957$), 12.1 days ($r^2 = 0.9786$), and 11.7 days ($r^2 = 0.9928$) following the four applications, respectively, calculated using linear regression analysis performed on a plot of ln-transformed penoxsulam concentrations vs. time and the equation $t_{1/2} = -ln\ 2 / k$, where k is the rate constant.

The mean measured penoxsulam concentration in water was initially 28.71-29.14 ng/mL at 0-1 days following the first application and decreased to 8.30 ng/mL by 27 days posttreatment, was initially 34.25 ng/mL immediately following the second application and decreased to 5.35 ng/mL by 28 days posttreatment, and was initially 24.63 ng/mL immediately following the third application and decreased to 5.58 ng/L by 27 days posttreatment (Table 23, p.148). Following the fourth application, penoxsulam was detected at a mean concentration of 26.27-27.47 ng/mL from 0 to 3 days, decreased to 13.13 ng/mL by 11 days, 4.99 ng/mL by 28 days, 0.85 ng/mL by 55 days, and was last detected at 0.01 ng/mL at 137 days posttreatment. Results showed that spatial distribution was accomplished by 3 days after each application (p.64; Table 22, pp.130-147). Mean penoxsulam concentrations at 3 days posttreatment ranged from 19.85 to 26.39 ng/mL or 99.3-132% of the target lake concentration. The study authors attributed the elevated concentration to sampling variability and incomplete mixing in the water column, and to the unknown size of the floating island below the surface which could have considerably reduced the total volume of water in the test system (pp.66-67). Vertical mixing was accomplished by 1-3 days posttreatment. Penoxsulam concentrations in water were corrected for the method recovery (p.63). Mean concentrations of penoxsulam residues in water are presented in the table below.

Penoxsulam concentrations in water, expressed as ng/mL.

Days posttreatment	Average concentration (ng/mL)	Range (mid water column depth)	Range (25 cm above sediment)
Application 1			
0	28.71	4.17-78.9	3.97-45.2
1	29.14	18.0-41.0	15.8-45.5
3	26.28	25.6-33.7	22.1-26.0
7	21.83	20.1-23.6	20.7-22.9
10	20.67	19.1-22.7	18.1-23.2
20	13.26	11.8-13.8	12.0-14.3
27	8.30	7.64-9.13	6.92-8.92
Application 2			
0	34.25	8.02-126	8.59-45.6
1	29.80	24.6-35.0	21.4-38.9

3	25.59	24.3-27.8	22.6-26.7
7	19.79	19.2-20.5	19.4-20.4
10	16.96	16.3-17.2	16.6-17.5
20	9.63	8.98-9.67	4.86-18.5
28	5.35	5.23-5.60	4.94-5.52
Application 3			
0	24.63	12.8-44.6	7.33-35.9
1	23.15	20.2-29.6	19.1-26.3
3	19.85	19.4-20.8	16.3-20.8
7	17.29	16.4-19.2	14.8-18.6
11	14.90	12.3-17.6	13.6-16.9
20	6.77	4.88-13.4	6.27-6.91
27	5.58	4.57-10.6	4.38-5.92
Application 4			
0	26.27	3.76-104	4.15-46.0
1	27.47	2.32-36.1	21.7-35.7
3	26.39	11.3-34.3	19.4-28.7
7	16.73	3.15-18.6	14.4-19.7
11	13.13	7.40-14.6	9.04-14.6
21	8.38	6.02-8.76	7.90-8.66
28	4.99	1.88-5.15	4.62-5.12
43	1.33	0.796-1.46	1.06-1.74
55	0.85	0.665-0.963	0.614-1.02
83	0.12	0.0879-0.179	0.0731-0.153
109	0.05	0.0500-0.0607	0.0479-0.0580
137	0.01	ND-0.0212	ND-0.0255
167	ND	ND	ND
210	ND	ND	ND-0.0176

Data were obtained from Tables 22-23, pp.130-148 of the study report. ND = Not detected.

The analysis of water samples from the three sampling stations established within the emergent vegetation zone of the lake indicated that penetration into the emergent zone was observed, with concentrations approaching equilibrium between the three stations at approximately 10 days following application (pp.64-65; Table 24, p.149). Concentrations were highest at sampling station J located in open water on the edge of the emergent zone, with concentrations ranging from 7.96-31.6 ng/mL from 0 to 7 days posttreatment, and lowest at sampling station L near the northern shoreline, with concentrations ranging from 2.32-11.3 ng/mL from 0 to 7 days. By 10 days, concentrations at all stations ranged from 7.40-14.2 ng/mL and by 21 days, concentrations ranged from 6.02-8.72 ng/mL.

Penoxsulam dissipated in the sediment with calculated half-lives of 8.2 days ($r^2 = 0.9046$), 12.9 days ($r^2 = 0.7256$), 7.8 days ($r^2 = 0.7225$), and 21.7 days ($r^2 = 0.7019$) following the four applications, respectively, calculated using linear regression analysis performed on a plot of ln-transformed penoxsulam concentrations vs. time and the equation $t_{½} = -ln\ 2 / k$, where k is the rate constant.

Penoxsulam concentrations in sediment mirrored those seen in the water (p.68). The mean measured penoxsulam concentration in sediment was initially 10.86 ng/g at 1 day following the first application and decreased to 0.80 ng/g by 27 days posttreatment, was initially 2.94 ng/g immediately following the second application and decreased to 0.81 ng/g by 28 days posttreatment, and was initially 6.96 ng/g immediately following the third application and decreased to 0.51 ng/g by 27 days posttreatment (Table 26, p.158). Following the fourth application, penoxsulam was detected at a mean concentration of 2.13 ng/g at 1 day, was a maximum of 3.75 ng/g at 3 days, then decreased to 1.53 ng/g by 21 days, and was last detected above the LOD at 1.18 ng/g at 28 days.

Penoxsulam concentrations in sediment, expressed as ng/g.

Days posttreatment	Average concentration (ng/g)	Range (ng/g)
Application 1		
1	10.86	3.14-29.9
3	3.82	1.84-5.51
7	4.09	1.36-12.9
10	3.57	2.16-6.22
20	1.46	ND-2.78
27	0.80	ND-2.87
Application 2		
1	2.94	1.42-9.89
3	5.02	ND-13.2
7	3.08	1.95-4.14
10	4.51	2.41-6.15
20	2.11	ND-4.83
28	0.81	ND-3.01
Application 3		
1	6.96	ND-16.7
3	4.55	1.65-10.5
7	0.85	ND-1.97
11	2.28	ND-8.81
20	0.74	ND-2.54
27	0.51	ND-2.09
Application 4		
1	2.13	ND-3.73
3	3.75	ND-8.41
7	2.26	ND-5.97
11	2.60	1.57-7.31
21	1.53	ND-2.82
28	1.18	ND-3.13
43	ND	ND
55	ND	ND
83	ND	ND
109	ND	ND
137	ND	ND
167	ND	ND
210	ND	ND

Data were obtained from Tables 25-26, pp.150-158 of the study report and from Appendix E, Table 9, pp.567-568, due to missing data from Table 25. ND = Not detected.

Total rainfall during the 9.5-month study period was 136.43 cm or 127% of the pro-rated annual historical rainfall total (pp.55-56); the unusually high rainfall total was the result of rainfall from three tropical storms. The lowest monthly rainfall total occurred in January 2005 (2.67 cm over 27 days), and the highest occurred in September 2004 (43.11 cm) and included 12.17 cm on September 6, 2004 (Appendix A, pp.186-195). Lake water levels ranged from a low of 121.2 cm on August 10, 2004 to a maximum of 177.2 cm on January 15, 2005 (p.60). Mean air temperatures were slightly above normal for the study period. Water temperatures monitored via a thermocouple stack ranged from a low of 8.58°C on December 27 and 28, 2004 (measured at 25 and 50 cm from the sediment) to a high of 34.55°C on August 6, 2004 (measured at 90 cm from the lake surface; p.57); the authors stated that the temperature gradient was very small and that no temperature stratification was apparent. Water temperatures, as measured by the Datasonde, showed similar results (p.58; Figure 14, p.173); temperatures followed a diurnal pattern with temperatures highest in the late afternoon due to solar warming (Figure 15, p.173).

The pH of the lake ranged from approximately 6 to 7.5 during the study period, with the exception of a spike to approximately 8 in mid September 2004 (p.58; Figure 16, p.174). Dissolved oxygen (DO) levels ranged from a low of approximately 0.6 mg/L to a high of 13.5 mg/L (p.59; Figure 18, p.175). The lowest DO levels were observed between September 30 and October 4, 2004, corresponding to the landfall of tropical storm Jeanne. Both pH and DO levels exhibited a diurnal pattern, with levels affected by the photosynthetic activity within the lake (Figures 17 and 19, pp.174-175). The authors stated that water quality parameters were typical of Florida lakes (p.61). The authors stated that water conductivity was low, ranging from 0.03 to 0.05 mS/cm (p.59; Figures 20-21, p.176). Light penetration measurements indicated that 74% of the UV-B light was extinguished in the top 2 cm of the water column, and 98% was extinguished in the top 10 cm (p.61; Table 18, p.124); Secchi readings showed visibility dropping from an average visibility limit of 136 cm over the first month of the study to 77 cm for the remainder of the study (Table 19, p.125; Figure 26, p.180). The authors stated that the readings indicated that the lake moved from a eutrophic state (high level of biological productivity) to a hypereutrophic state (extremely high level of biological productivity) during the course of the study (p.61).

The storage stability study MRID 46433901 indicated that penoxsulam declined slightly in stored samples but that penoxsulam was stable for at least 230 days in water. Mean corrected recoveries of penoxsulam from fortified water samples stored in the refrigerator were 109% at day 0, 111% at 101 days, 101% at 230 days, and 93% following 433 days. Mean corrected recoveries from fortified water samples stored frozen were 109% at day 0, 96% at 221 days, and 61% at 320 days. The storage stability study MRID 46433902 indicated that penoxsulam was stable in frozen soil for the duration of the 781-day storage interval, with corrected recoveries ranging from 80-97%.

Results from the storage stability study of penoxsulam in test water (determined by re-analyzing water samples collected from sampling stations A and H at 7 days posttreatment of the fourth application) indicated that penoxsulam degraded slightly over the storage interval. However, the results are questionable due to the poor design of the storage stability study (no time-0 analysis was conducted). Recoveries of penoxsulam from sampling station A were initially 21.1-22.3

ng/mL at 75 days of storage and were 15.8-16.2 ng/mL following 190 days of storage (Table 20, p.126). Recoveries of penoxsulam from sampling station H were initially 18.3-18.4 ng/mL at 75 days of storage and were 15.2-15.4 ng/mL following 190 days of storage (Table 20, p.127). Results are presented graphically in Figure 27 (p.181).

STUDY DEFICIENCIES

1. The maximum proposed single use rate was not used in the study. The study authors stated that the study was designed to determine the pattern of penoxsulam dissipation when maintained at a water concentration of not less than 5 µg/L for a 4-month period (p.15). This minimum concentration was achieved through four applications of penoxsulam (at approximately 28-day intervals) to bring the nominal whole lake concentration to 20 µg penoxsulam/L (pp.33-34). However, the maximum proposed single use rate was reported as 150 µg/L (p.18). The study authors stated that current efficacy data indicate that cost-effective hydrilla control can be achieved by maintaining a penoxsulam water concentration of 5-20 µg/L for the 3-4 month period at the beginning of the annual growing season (p.16). However, the authors did not use this as justification for the decreased application rate. The EPA Guideline 164-2 requires that the test substance be applied at the highest recommended label rate. A separate aquatic dissipation study of penoxsulam (MRID 46703502) was conducted on a 0.9-ha pond using a single subsurface application to achieve a whole-water body concentration of 150 µg/L.

2. No attempt was made to identify transformation products of penoxsulam. The study authors stated that transformation products were not monitored because the application rate utilized was not near the proposed 150 µg/L maximum single use rate. The reviewer notes that EPA Guideline 164-2 requires that a reasonable attempt be made to identify any transformation products that exceed the lower of 10% of the initial concentration of the parent or 0.01 ppm. A separate aquatic dissipation study of penoxsulam (MRID 46703502) was conducted at the maximum proposed label rate, and included analysis of water samples for seven transformation products of penoxsulam and analysis of sediment samples for five transformation products of penoxsulam.

REVIEWER'S COMMENTS

1. It is interesting to note that average measured concentrations (23.3 to 29.8 µg/L) 24 hours after application were 17% to 49% higher than the targeted whole-lake concentrations of 20 µg/L. This observation suggests that, in actual usage, initial concentrations of penoxsulam may exceed the intended applied concentration, and therefore might, in some places, inadvertently exceed maximum labeled concentrations for short periods following application at maximum application rates. Extrapolating the 17% and 49% exceedence of the target concentration of 150 µg/L reveals the possibility of short-term aquatic concentrations ranging from 176 to 224 µg/L.

2. There was no pesticide use history for the test site. A three-year use history is needed to determine if pesticides related to the test chemical were applied in recent years that could have affected the degradation rate of the test chemical.

3. The water solubility of penoxsulam is pH dependent, ranging from 0.0057 g/L at pH 5 to 1.46 g/L at pH 9 (pp.16-17; Table 1, p.86). Vapor pressure of penoxsulam is 9.55×10^{-14} Pa at 25°C and 2.49×10^{-14} Pa at 20°C. Adsorption Koc values range from 12 to 1141 L/Kg, indicating that penoxsulam may be considered potentially mobile to immobile; penoxsulam sorption is not dependent upon concentration.

4. The study authors stated that data gaps due to equipment malfunction of the on-site automated weather station were supplemented with data from three other sources. A station installed approximately 6 kilometers from the test site for use in a companion study; a NOAA weather station (station id 085275) located approximately 8 kilometers from the test site, and a NOAA station (station id 084394) located approximately 38 kilometers from the test site (pp.28-29).

5. The study authors stated that penoxsulam degradation proceeds via cleavage of the sulfonamide bridge (photolysis) and through breakage of the pyrimidine ring (biological degradation; p.17).

5. It was stated that instrumentation to measure the oxidation-reduction potential of the bottom sediment was installed at sampling station A, but that data were not reported because the sensors failed at 18 days after the first test application, and the oxidation-reduction monitoring equipment was removed (pp.30-31).

6. Application equipment calibration data reported in Table 6 (p.91) of the study report show that the relative standard deviation determined during four output checks (one for each application) ranged from 0.75-1.05% (p.35).

8. A laboratory study on the stability and uniformity of penoxsulam (SC formulation) when mixed with water and adjuvant (Agri-Dex crop-oil-concentrate) was previously

conducted (p.38). The results indicated that penoxsulam was uniformly distributed in the tank and was chemically stable for more than 12 hours in the tank mixture.

REFERENCES

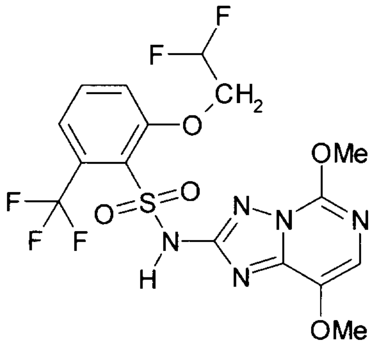
1. U.S. Environmental Protection Agency. 1982. Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate, Section 164-1, Terrestrial Field Dissipation Studies. Office of Pesticide and Toxic Substances, Washington, DC. EPA 540/9-82-021.

2. U.S. Environmental Protection Agency. 1993. Pesticide Registration Rejection Rate Analysis - Environmental Fate. Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 738-R-93-010.

3. U.S. Environmental Protection Agency. 1989. FIFRA Accelerated Reregistration, Phase 3 Technical Guidance. Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 540/09-90-078.

Penoxsulam [XDE-638; DE-638; TSN101649; SP1019 (SePRO)]

IUPAC Name:	3-(2,2-Difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-α,α,α-trifluorotoluene-sulfonamide. 2-(2,2-Difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide. 6-(2,2-Difluoroethoxy)-N-(5,8-dimethoxy-s-triazolo[1,5-c]pyrimidin-2-yl)-α,α,α-trifluoro-o-toluenesulfonamide.
CAS Name:	2-(2,2-Difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide.
CAS Number:	219714-96-2.
SMILES String:	FC(c1cccc(c1S(=O)(=O)N(c1nn2c(n1)ccnc2))OCC(F)F)(F)F (ISIS v2.3/Universal SMILES). No EPI Suite, v3.12 SMILES String found as of 6/27/06. n1c(nc2n1c(ncc2OC)OC)NS(=O)(=O)c3c(cccc3C(F)(F)F)OCC(F)F.

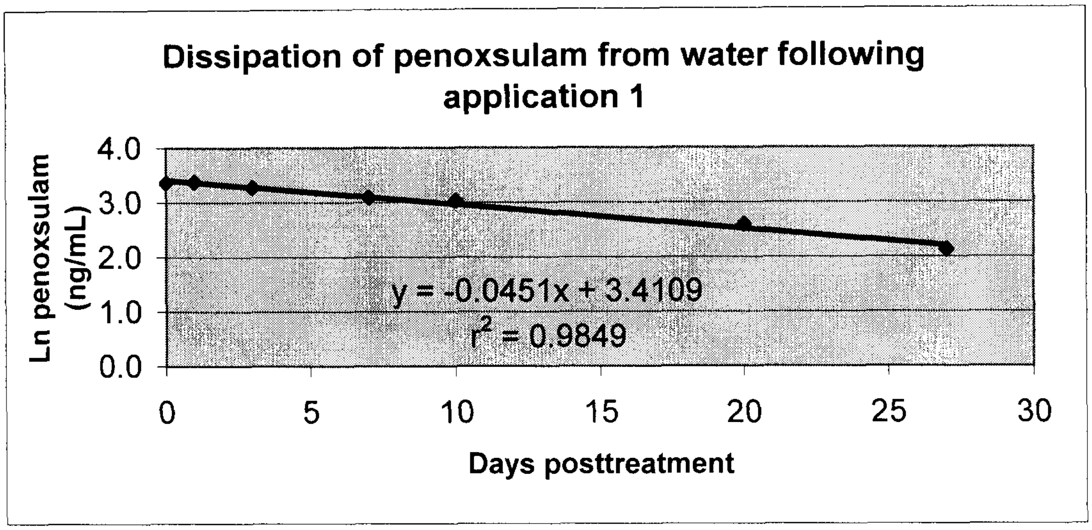


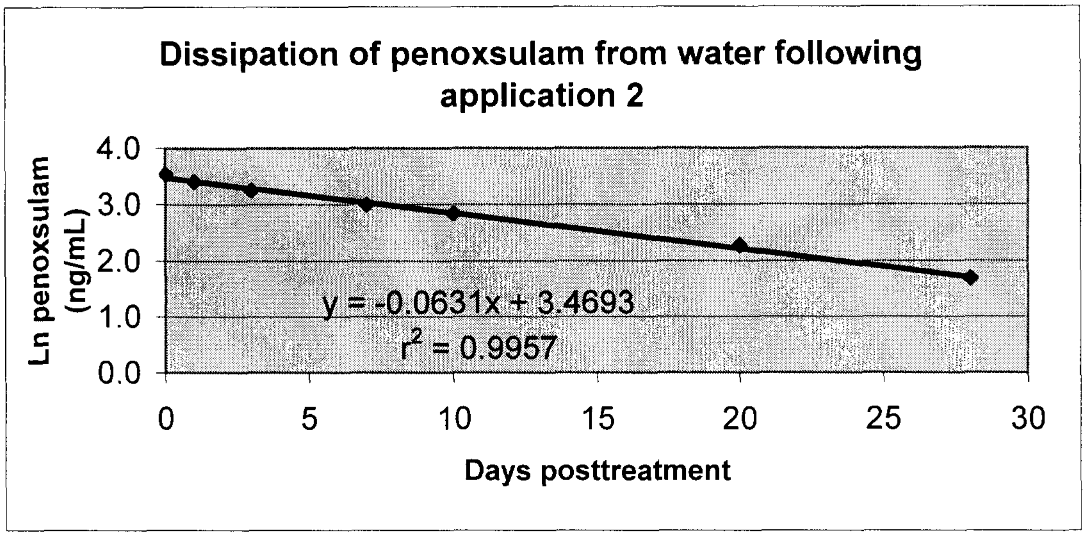
Attachment 2: Excel Spreadsheets

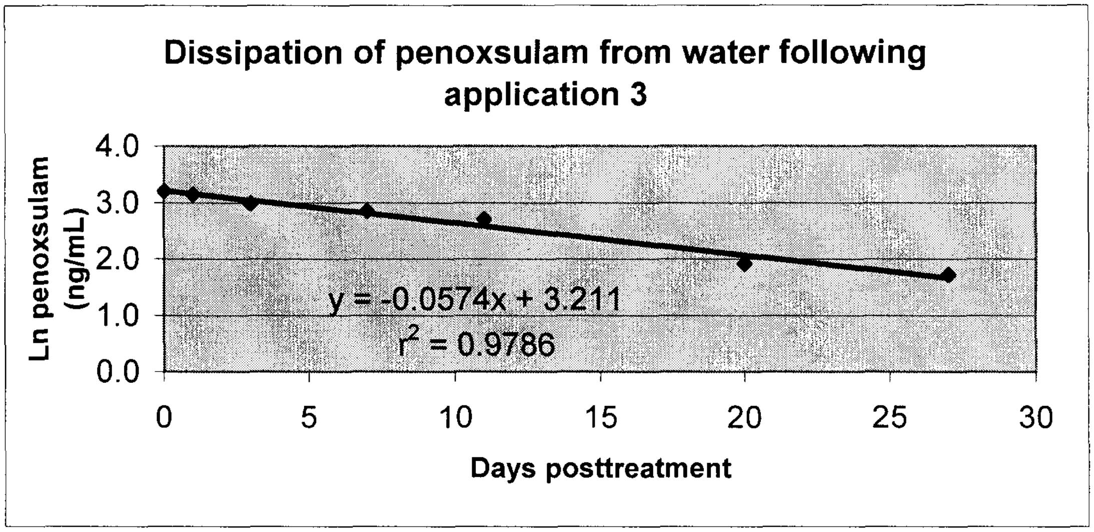
Chemical name	Penoxsulam	**Water**
PC code	119031	
MRID	46703503	
Guideline No.	164-2	

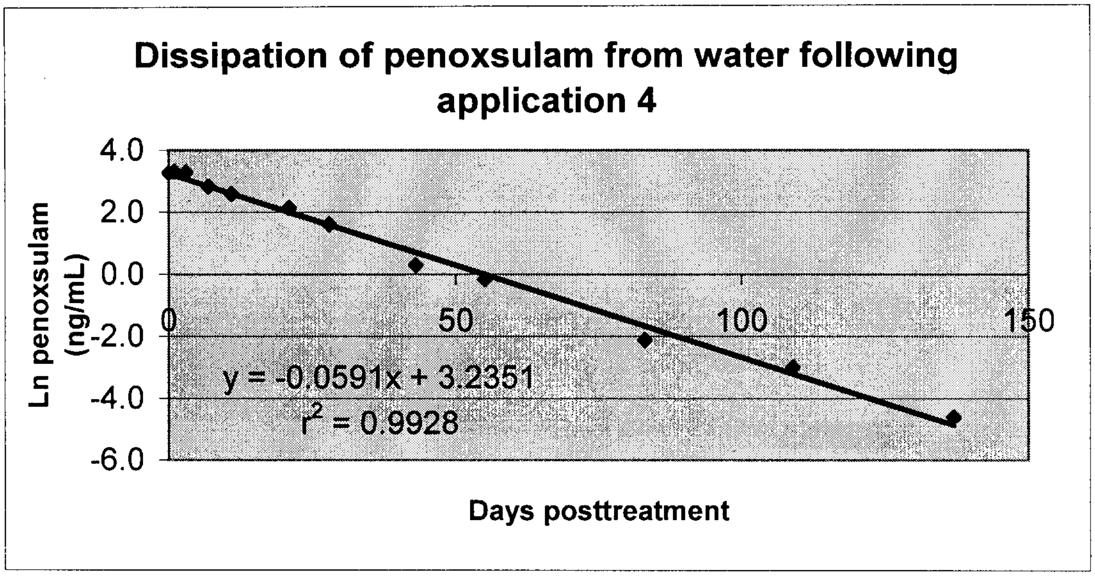
Days posttreatment	Penoxsulam (ng/mL)	Ln (penoxsulam)	**Half-life (days)**
Application 1			**15.4**
0	28.71	3.36	
1	29.14	3.37	
3	26.28	3.27	
7	21.83	3.08	
10	20.67	3.03	
20	13.26	2.58	
27	8.30	2.12	
Application 2			**11.0**
0	34.25	3.53	
1	29.80	3.39	
3	25.59	3.24	
7	19.79	2.99	
10	16.96	2.83	
20	9.63	2.26	
28	5.35	1.68	
Application 3			**12.1**
0	24.63	3.20	
1	23.15	3.14	
3	19.85	2.99	
7	17.29	2.85	
11	14.90	2.70	
20	6.77	1.91	
27	5.58	1.72	
Application 4			**11.7**
0	26.27	3.27	
1	27.47	3.31	
3	26.39	3.27	
7	16.73	2.82	
11	13.13	2.57	
21	8.38	2.13	
28	4.99	1.61	
43	1.33	0.29	
55	0.85	-0.16	
83	0.12	-2.12	
109	0.05	-3.00	
137	0.01	-4.61	

* Data obtained from Table 23, p. 148 of the study report.


Dissipation of penoxsulam from water following application 1
Ln penoxsulam (ng/mL)
4.0
3.0
2.0
1.0
0.0
y = -0.0451x + 3.4109
r2 = 0.9849
0
5
10
15
20
25
30
Days posttreatment


Dissipation of penoxsulam from water following application 2
Ln penoxsulam (ng/mL)
4.0
3.0
2.0
1.0
0.0
y = -0.0631x + 3.4693
r2 = 0.9957
0
5
10
15
20
25
30
Days posttreatment

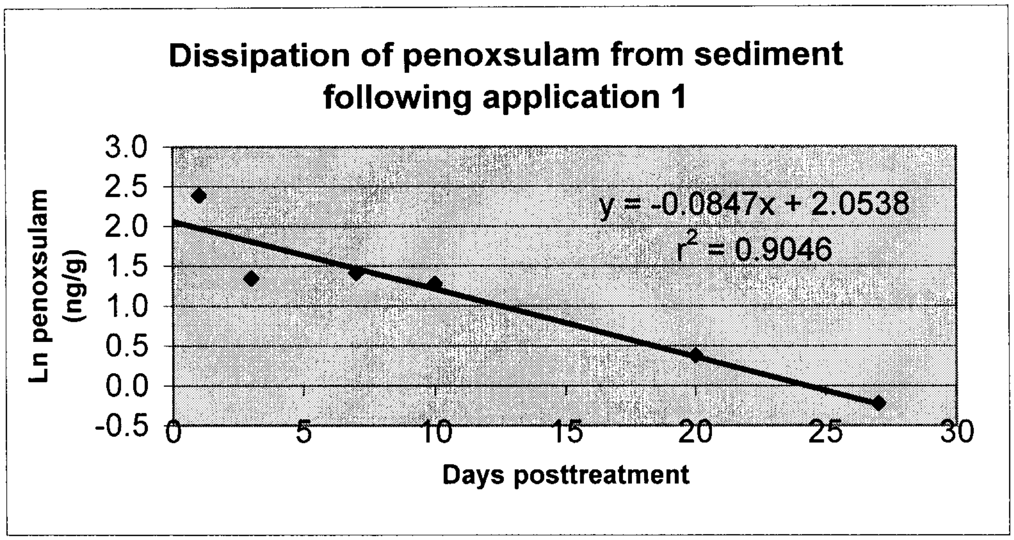

Dissipation of penoxsulam from water following application 3
Ln penoxsulam (ng/mL)
4.0
3.0
2.0
1.0
0.0
y = -0.0574x + 3.211
r2 = 0.9786
0
5
10
15
20
25
30
Days posttreatment


Dissipation of penoxsulam from water following application 4
Ln penoxsulam (ng/mL)
4.0
2.0
0.0
-2.0
-4.0
-6.0
0
50
100
150
y = -0.0591x + 3.2351
r² = 0.9928
Days posttreatment

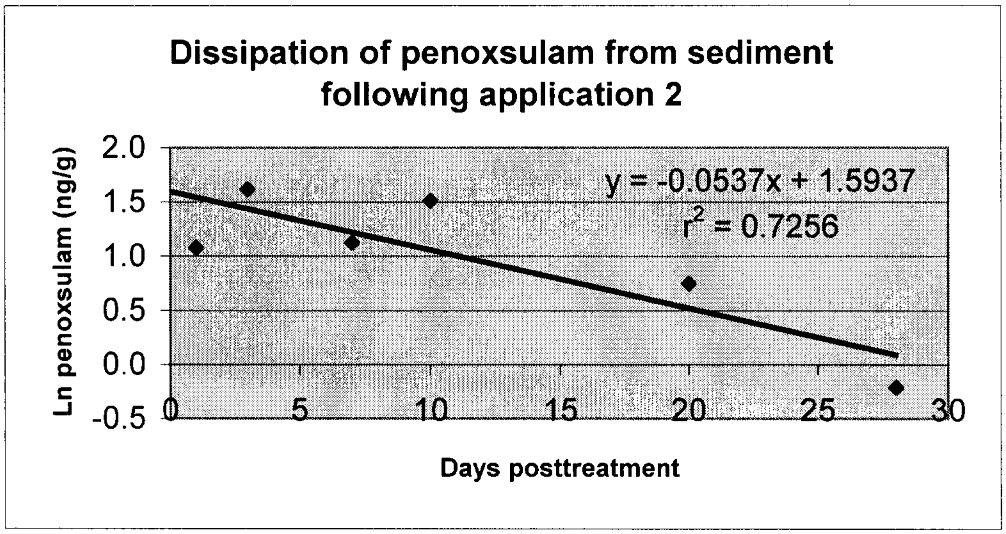
Chemical name	Penoxsulam		**Sediment**
PC code	119031		
MRID	46703503		
Guideline No.	164-2		

Days posttreatment	Penoxsulam (ng/g)	Ln (penoxsulam)	**Half-life (days)**
Application 1			**8.2**
0	No sample		
1	10.86	2.39	
3	3.82	1.34	
7	4.09	1.41	
10	3.57	1.27	
20	1.46	0.38	
27	0.80	-0.22	
Application 2			**12.9**
0	No sample		
1	2.94	1.08	
3	5.02	1.61	
7	3.08	1.12	
10	4.51	1.51	
20	2.11	0.75	
28	0.81	-0.21	
Application 3			**7.8**
0	No sample		
1	6.96	1.94	
3	4.55	1.52	
7	0.85	-0.16	
11	2.28	0.82	
20	0.74	-0.30	
27	0.51	-0.67	
Application 4			**21.7**
0	No sample		
1	2.13	0.76	
3	3.75	1.32	
7	2.26	0.82	
11	2.60	0.96	
21	1.53	0.43	
28	1.18	0.17	
43	Not detected		

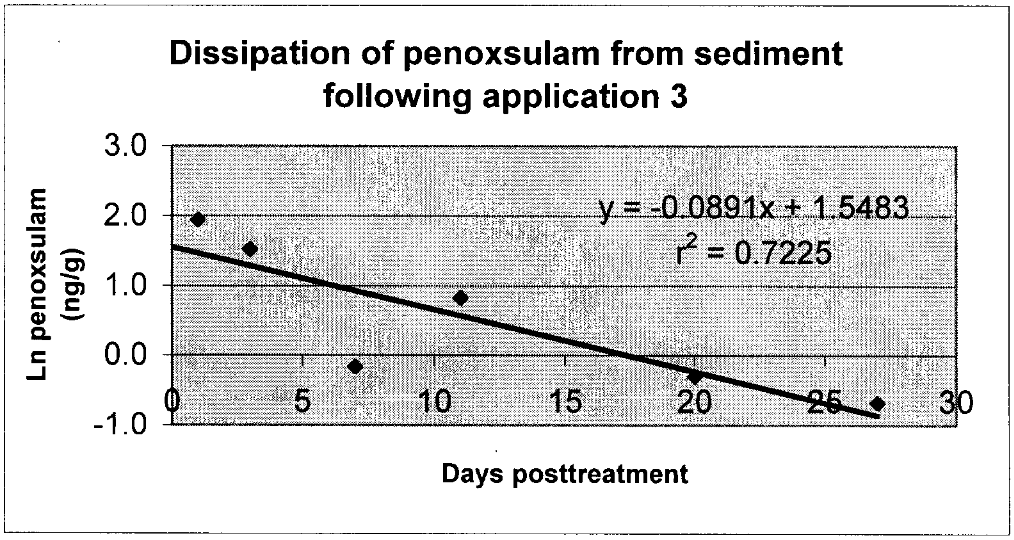
* Data obtained from Table 26, p. 158 of the study report.



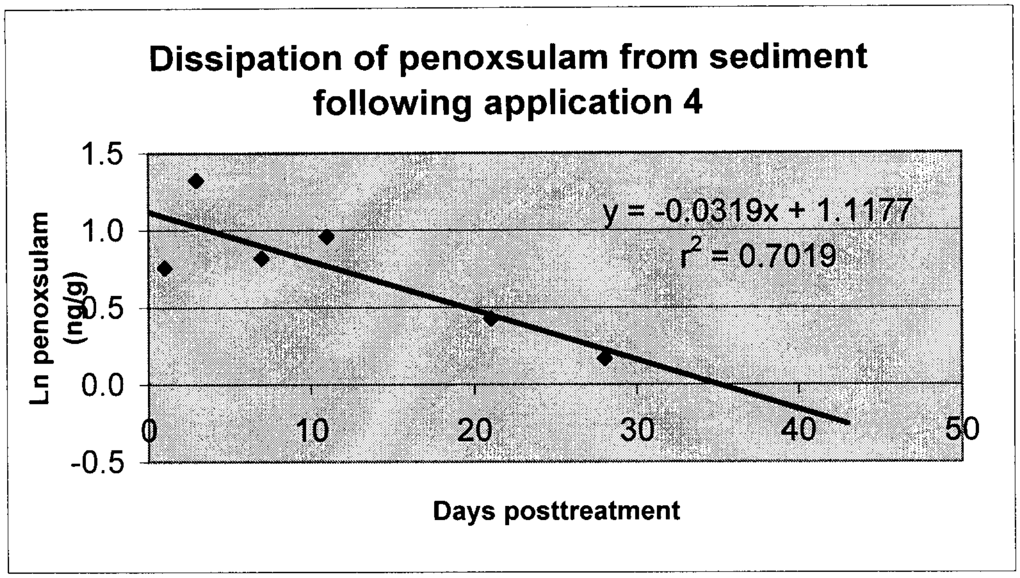
Dissipation of penoxsulam from sediment following application 1



Dissipation of penoxsulam from sediment following application 2



Dissipation of penoxsulam from sediment following application 3



Dissipation of penoxsulam from sediment following application 4
y = -0.0319x + 1.1177
r2 = 0.7019
Ln penoxsulam (ng/g)
1.5
1.0
0.5
0.0
-0.5
0
10
20
30
40
50
Days posttreatment