3-18-99

DATA EVALUATION RECORD

STUDY 5a

CHEM 005108, 005107 Diflufenzopyr (SAN 835H) §164-1
CAS No. 109293-97-2
FORMULATION--06--WETTABLE POWDER

STUDY ID 44329605
Clouser Roche, A. R. 1997. SAN 835H field soil dissipation - OH. Project No.: 414208. BASF Reg. Doc. No. 97/5152. Study completion date, April 2,1997. Unpublished study performed by Ag Consultants, Inc., New Holland, OH (in-life phase), and Sandoz Agro, Inc., Des Plaines, IL (analytical phase); and submitted by Sandoz Agro, Inc., Des Plaines, IL.

STUDY ID 44329606
Marquardt, L. A. and A. R. Clouser Roche. 1997. SAN 835H field soil dissipation - IN. Project No.: 414208. BASF Reg. Doc. No. 97/5157. Study completion date, April 2,1997. Unpublished study performed by Heartland Technologies, Inc., Noblesville, IN (in-life phase), and Sandoz Agro, Inc., Des Plaines, IL (analytical phase); and submitted by Sandoz Agro, Inc., Des Plaines, IL.

STUDY ID 44307411
Megli, D. 1997. SAN 835H field soil dissipation - CA. Project No.: 414208. BASF Reg. Doc. No. 97/5101. Study completion date, April 28,1997. Unpublished study performed by Western Ag Research, Suisun, CA (in-life phase), and Sandoz Agro, Inc., Des Plaines, IL (analytical phase); and submitted by Sandoz Agro, Inc., Des Plaines, IL.

STUDY ID 44307412
Ballentine, R. J. and A. R. Clouser Roche. 1997. SAN 835H field soil dissipation - NE. Project No.: 414208. BASF Reg. Doc. No. 97/5148. Unpublished study performed by Midwest Research Inc., York, NE (in-life phase), and Sandoz Agro, Inc., Des Plaines, IL (analytical phase); and submitted by Sandoz Agro, Inc., Des Plaines, IL.

STUDY ID 44307420
Carrier, M. N. 1996. Validation of the analytical method for the determination of SAN 835H and its phthalazinone residues (M1 and M5 metabolites) in soil, 1995. Project No.: R95-034. BASF Reg. Doc. No. 97/5142. Unpublished study performed by Sandoz Agro Europe, Huningue Cedex, FRANCE; and submitted by Sandoz Agro, Inc., Des Plaines, IL.

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DIRECT REVIEW TIME = 223.5 Hours

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CONCLUSIONS

Field Dissipation - Terrestrial

1. This study is unacceptable because it was done with the technical ingredient rather than the formulated product. In addition, the storage stability and method validation studies were inadequate. The method validation study for diflufenzopyr and its degradates M1 and M5 (BASF #97/5142) was not the same method utilized in the four U.S. field dissipation studies reviewed for this assessment. In the submitted analytical method, M5 was converted to M1 during the analytical procedure and was detected as M1. This method did not analyze for all of the other major diflufenzopyr metabolites.

2. The registrant needs to submit at least three field studies using the formulated product in areas that are representative of the use area. EPA recommends that the field studies be conducted in Nebraska, Ohio or Indiana, and California or Florida. Diflufenzopyr and dicamba plus their major metabolites need to be monitored in these studies. Because of the mode of action of the end-use product BAS 662H 70WG (diflufenzopyr enhances the toxicity of dicamba in plants) determination of the field dissipation of both parent active ingredients and their major degradates is necessary for the evaluation of environmental risk to nontarget plants and other organisms, and for the evaluation of the potential alteration in environmental fate parameters, such as soil aerobic metabolism, when both active ingredients are present in the environment.

3. Diflufenzopyr dissipated in silt loam soil in Ohio, loam soil in Indiana, sandy loam soil in California, and silty clay loam soil in Nebraska, with respective registrant-calculated half-lives of 5.2, 3.5, 6.1 and 3.3 days in bare ground plots. Half-life calculations were based on nonlinear first order regression analysis. At the Ohio, Indiana, California and Nebraska sites, the parent compound was initially (day 0) present in the 0- to 10-cm depth at maximums of 0.090, 0.131, 0.051 and 0.159 ppm, respectively, and was not detected by 32, 29, 29 and 29 days posttreatment, respectively. The parent compound was not detected below the 10-cm depth at the Indiana and California sites. At the Ohio and Nebraska sites, parent compound was observed below the 10-cm depth once per site, at 0.016 ppm at 14 days posttreatment (20- to 30-cm depth) and at 0.011 ppm at 4 days posttreatment (20- to 30-cm depth), respectively. The degradate M1 was observed in the 0- to 10-cm depth at the California and Nebraska sites at maximums of 0.017 ppm (88 days) and 0.014 ppm (29 days), respectively; M1 was not detected below the 10-cm depth. The expected degradate M1 was not detected in the soil at the Ohio and Indiana sites. The degradate M9 (2-Keto M1) was only analyzed for in selected samples in Ohio, California and Indiana. M9 was detected in the 0- to 10-cm depth at the Indiana and California sites at maximums of 0.019 ppm (361 days) and 0.012 ppm (355 days), respectively; M9 was not detected below the 10-cm depth. The expected degradate M9 was not detected in the soil at the Ohio site. Analyses for M9 were not performed on soil samples from the Nebraska site.

METHODOLOGY

New Holland, Ohio (44329605)

Diflufenzopyr (SAN 835H; WP, 86% a.i.) was broadcast applied once (CO_2 backpack sprayer equipped with six flat fan nozzles) as a spray at a nominal rate of 0.2 lb a.i./A onto bare ground test plots (3 plots of 20 x 110 feet with 18 subplots of 20 x 6 feet; ~1% slope) of silt loam soil (26% sand, 54% silt, 20% clay, 1.9% organic matter, pH 6.2, CEC 12.4 meq/100 g); SAN 835H was applied as SAN 836H (the sodium salt of SAN 835H). A control plot (20 x 110 feet) was located 50 feet from the treated plots. The application rate was *not* verified by soil monitoring pads or other valid means; however, based on the theoretical value (0.192 ppm) reported by the registrant, the parent compound was present at 47% (day 0) of the expected soil concentration in the 0- to 10-cm depth. Precipitation was supplemented with irrigation (sprinkler); total water input via precipitation and irrigation was 112% (reviewer calculated) of the historical average for the months of June through December (Table 4; see Comment #13). The time period length from which the historical precipitation average was determined was not reported. A five-year plot history indicated no prior use of diflufenzopyr (Table 2). The test plot was treated during the in-life phase of the test with Gramoxone (paraquat) and Frontier (Table 3). The depth to the water table was greater than 3 feet (see Comment #16). Environmental data were collected onsite for the months of June through December 1995 (Table 4; see Comment #13); August temperature data were collected offsite. Daily air and soil temperatures, humidity, precipitation and irrigation throughout the study were reported in the field study notebook (submitted report p. 15); data were not submitted. Pan evaporation data were not reported.

Soils were sampled one day prior to application and at 0, 1, 2, 4, 7, 14, 32, 48, 61, 88, 120, 293, 358 and 543 days posttreatment; control plot samples were collected one day prior to application and at 0, 7, 32, 61, 120, 358 and 543 days posttreatment. Eight soil cores were removed from a random subplot in each plot; a two-phase, acetate sleeve-lined, Concord hydraulic soil probe mounted on a tractor was used to collect a 0- to 10-cm depth soil sample (2.25-inch i.d.) and a 10- to 90-cm soil sample (2-inch i.d.). Pretreatment and control samples were collected as a single 0- to 90-cm depth sample (2-inch i.d.). All samples were placed in a freezer (≤0 °F) within one hour of collection. Samples were transported frozen by refrigerated carrier to the analytical laboratory; samples collected one day prior to treatment were transported by "common carrier." Soil cores were sectioned into 10-cm depth increments and composited by subplot and depth.

Diflufenzopyr and the degradate M1 {8-methylpyrido[2,3-d]pyridazin-5(6H)-one; phthalazinone} were extracted from the soil samples by shaking with 0.5% aqueous sodium bicarbonate solution:acetone (1:3, v:v) followed by centrifugation and filtration (Appendix III). The acetone was evaporated and the remaining aqueous portion was

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partitioned three times with dichloromethane. The organic phase containing M1 was filtered through sodium sulfate, evaporated to dryness and reconstituted in toluene prior to analysis by GC (Restek XTI-5 column) with N/P detection; the limit of quantitation was 0.015 ppm (report p. 16). The aqueous layer was acidified (HCl) and partitioned three times with dichloromethane. The organic phase containing diflufenzopyr was filtered through sodium sulfate, evaporated to dryness, redissolved in 1% aqueous Na_2CO_3:20% acetonitrile in water (1:100, v:v) prior to HPLC analysis (Alltech Alltima C18 column) with a mobile phase of 0.05 M aqueous acetic acid:0.05 M acetic acid in acetonitrile (60:40, v:v) and UV (240 nm) detection (p. 113); the limit of quantitation was 0.034 ppm (report p. 16). The degradate M9 (2-Keto M1) {8-methylpyrido[2,3-d]pyridazine-2,5(1H,6H)-dione} was analyzed for only in selected samples; no samples were analyzed for M9 until 32 days posttreatment in the 0-10 and 10-20 cm depth range, and 88 days posttreatment in the 20-30 cm range. In these samples M9 was extracted from the soil samples by shaking twice with methanol:1% acetic acid in water (3:1, v:v) followed by centrifugation and filtration (Appendix IV, p. 153). The combined extracts were evaporated, diluted with deionized water and filtered prior to HPLC analysis (Alltech Alltima C18 column) with a mobile phase of 0.1% trifluoroacetic acid in water:0.1% trifluoroacetic acid in acetonitrile (93:7, v:v) and UV (240 nm) detection (p. 155); the limit of quantitation was 0.010 ppm (report p. 17). No analyses for M5, another major degradate and the reported precursor to M1, were conducted. [In the soil aerobic laboratory metabolism study (MRID 44170153) submitted by the registrant, it was reported that M5 attained a maximum level of 20% of the applied at day 14 posttreatment, and is therefore a significant degradate.] At least one control plot sample and one fortified sample were analyzed concurrently with each set of samples.

Concurrent recoveries for 0- to 10-cm depth samples fortified separately at 0.01-0.1 ppm with diflufenzopyr and the degradates M1 and M9 were 81-111%, 72-101% and 62-87%, respectively (Tables 13-15); recoveries from the 10- to 20-cm and 20- to 30-cm depths were also reported.

In a previous study (MRID 44329606), diflufenzopyr and M1 were determined to be stable in loam soil in frozen storage for up to 317 days (report p. 16; see Comments #2, 12); data were not reported. Study samples analyzed for diflufenzopyr and M1 were placed in frozen storage for less than six months prior to analysis (Tables 10-11. Storage stability data were not for submitted for the silt loam soil or for the degradate M9 (2-keto M1).

Noblesville, Indiana (44329606)

Diflufenzopyr (SAN 835H; WP, 86% a.i.) was broadcast applied once as a spray at a nominal rate of 0.2 lb a.i./A onto bare ground test plots (3 plots of 20 x 150 feet with 15 subplots of 8 x 20 feet; 1% slope) of loam soil (32% sand, 41% silt, 27% clay, 3.8% organic matter, pH 6.2, CEC 23.5 meq/100 g; Table 1); SAN 835H was applied as SAN

836H (the sodium salt of SAN 835H). A control plot (20 x 150 feet) was located 60 feet upslope from the treated plots (report p. 13). The application rate was not verified by soil monitoring pads or other valid means; however, based on the theoretical value (0.208 ppm) reported by the registrant, the parent compound was present at 63% (0 day) of the expected soil concentration in the 0- to 10-cm depth. Precipitation was supplemented with irrigation; total water input via precipitation and irrigation was 119% (reviewer calculated) of the 10-year historical precipitation average for the months of June through December (Table 4; see Comment #13). A five-year plot history indicated no prior use of diflufenzopyr (Table 2). The test plot was treated during the in-life phase of the test with non-ionic surfactant three times, Gramoxone (paraquat) twice, Roundup 3SL (glyphosate) once and Bicep 6L once (Table 3); dead weeds were mowed twice during the in-life phase. The depth to the water table (seasonal high) was 6-8 feet. Environmental data were collected onsite for the months of June through December 1995 (Table 4, p. 28; see Comments #13 and #18). Daily air and soil temperatures, humidity, precipitation and irrigation throughout the study were reported in the field study notebook (report p. 15); daily data were not submitted. Pan evaporation data were not reported.

Soil cores were collected three days prior to application and at 0, 1, 2, 4, 14, 29, 45, 60, 88, 116, 178, 361 and 514 days posttreatment; control plot samples were collected three days prior to application and at 0, 7, 29, 60, 116, 361 and 514 days posttreatment. At each sampling interval, eight soil cores were removed from each plot as previously described for the Ohio site. All samples were placed in a freezer (≤0 °F) within two hours of collection. Samples were transported frozen by refrigerated carrier to the analytical laboratory; samples collected three days prior to treatment were transported by "common carrier." Soil cores were sectioned into 10-cm depth increments and composited by subplot and depth.

Diflufenzopyr and the degradates M1 {8-methylpyrido[2,3-d]pyridazin-5(6H)-one} and M9 {8-methylpyrido[2,3-d]pyridazine-2,5(1H,6H)-dione} were extracted and analyzed as described previously for samples collected from the Ohio site (Appendix III, pp. 115-119; Appendix IV, pp. 158-160). Analyses for the degradate M9 (2-Keto M1) {8-methylpyrido[2,3-d]pyridazine-2,5(1H,6H)-dione} were conducted with selected samples; no samples were analyzed for M9 until 29 days posttreatment. The limits of detection for diflufenzopyr, M1 and M9 were 0.013 ppm, 0.005 ppm and 0.003 ppm, respectively (report pp. 17-18). At least one control plot sample and one fortified sample were analyzed concurrently with each set of samples. Analyses were not conducted for the major degradate M5 , which attained a maximum level of approximately 20% of the applied in the soil aerobic metabolism study (MRID 44170153).

Concurrent recoveries for 0- to 10-cm depth samples fortified separately at 0.01-0.1 ppm with diflufenzopyr and the degradates M1 and M9 were 57-106%, 68-112% and 52-81%, respectively (Tables 13-15, pp. 45-51); recoveries from the 10- to 20-cm and 20- to 30-cm depths were also reported.

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In a transport and storage stability study, soil samples were fortified separately with diflufenzopyr and M1 at 0.1 ppm on the day of application and transported, stored and analyzed in the same manner as the test sample. Field fortified samples were compared to lab samples fortified on the day of analysis. Recoveries of diflufenzopyr and M1 following 317 days of storage were 74% and 120%, respectively; and were 3% and 0.5% different from the lab fortified samples (Table 16). Most of the study samples analyzed for diflufenzopyr and M1 were placed in frozen storage for less than 10 months (Tables 10-11); only day 178 samples analyzed for M1 were stored longer (approximately 1 year; Table 11). Storage stability data for M9 were not submitted.

Vacaville, California (44307411)

Diflufenzopyr (SAN 835H; WP, 86% a.i.) was broadcast applied once (backpack boom sprayer equipped with six nozzles) as a spray at a nominal rate of 0.2 lb a.i./A onto bare ground test plots (3 plots of 75 x 20 feet with 15 subplots of 5 x 20 feet; 2% slope) of sandy loam soil (60% sand, 21% silt, 19% clay, 1.1% organic matter, pH 6.5, CEC 14.4 meq/100 g); SAN 835H was applied as SAN 836H (the sodium salt of SAN 835H). A control plot, similar in size (unspecified dimensions) to the treated plots, was located 100 feet upslope from the treated plots. The application rate was not verified by soil monitoring pads or other valid means; however, based on the theoretical value (0.187 ppm) reported by the registrant (p. 20), the parent compound was present at 27% (0 day) of the expected soil concentration in the 0- to 10-cm depth (see Comment #19). The test plots were irrigated (sprinkler) once with 2.5 inches of water in July 1995 (Table 4); total water input via precipitation and irrigation was 134% (reviewer calculated) of the historical precipitation average for the months of July through December (see Comment #13). The test plots did not receive any precipitation or irrigation from September to November. The time period length from which the historical precipitation average was determined was not reported. A five-year plot history indicated no prior use of diflufenzopyr (Table 2). The test plot was treated during the in-life phase of the test with Roundup (glyphosate) five times and was hand weeded once (Table 3). The depth to the water table (seasonal high) was 9 feet. Temperature data were collected onsite for the months of July through December 1995 (Table 4; see Comment #13); rainfall data were collected offsite. Daily air and soil temperatures, humidity, precipitation and irrigation throughout the study were reported in the field study notebook (p. 15); daily data were not submitted. Pan evaporation data were not reported.

Soil cores were collected one day prior to application and at 0, 1, 2, 4, 7, 14, 29, 46, 61, 88, 231, 259, 355 and 596 days posttreatment; control plot samples were collected one day prior to application and at 0, 7, 29, 61, 231, 259, 355 and 596 days posttreatment. At each sampling interval, eight soil cores were removed from each plot as previously described for the Ohio site except that a Giddings, Inc. soil excavator was used in place of the Concord hydraulic soil probe. All samples were placed in a freezer (≤0 °F) within

two hours of collection. Samples were transported frozen by refrigerated carrier to the analytical laboratory; samples collected one day prior to treatment were transported by "common carrier." Soil cores were sectioned into 10-cm depth increments and composited by subplot and depth.

Diflufenzopyr and the degradates M1 {8-methylpyrido[2,3-d]pyridazin-5(6H)-one} and M9 (2-Keto M1) {8-methylpyrido[2,3-d]pyridazine-2,5(1H,6H)-dione} were extracted and analyzed as described previously for samples collected from the Ohio site (Appendix III; Appendix IV). The degradate M9 was assayed for only in selected samples; no samples were analyzed for M9 until 29 days posttreatment, and samples at the 20-30 cm depth were only analyzed for the presence of M9 on 3 sample collection days (days 61, 259 and 596 posttreatment). The limits of detection for diflufenzopyr, M1 and M9 were 0.007 ppm, 0.005 ppm and 0.004 ppm, respectively (report p. 17). At least one control plot sample and one fortified sample were analyzed concurrently with each set of samples. Analyses were not conducted for the major degradate M5, which attained a maximum level of approximately 20% of the applied in the soil aerobic metabolism study (MRID 44170153).

Concurrent recoveries for 0- to 10-cm depth samples fortified separately at 0.01-0.1 ppm with diflufenzopyr and the degradates M1 and M9 were 67-110%, 70-107% and 71-83%, respectively (Tables 13-15); recoveries from the 10- to 20-cm and 20- to 30-cm depths were also reported.

In a previous study (MRID 44329606), diflufenzopyr and M1 were determined to be stable in frozen storage for up to 317 days (see Comment #2); data were not reported. Study samples analyzed for diflufenzopyr and M1 were placed in frozen storage for approximately 9 months or less (Tables 10-11, see Comment #12); only day 231 samples analyzed for M1 were stored longer (approximately 1 year; Table 11). Storage stability data were not for submitted for the sandy loam soil or for the degradate M9.

York, Nebraska (44307412)

Diflufenzopyr (SAN 835H; WP, 86% a.i.) was broadcast applied once (boom sprayer equipped with eight flat fan nozzles) as a spray at a nominal rate of 0.2 lb a.i./A onto bare ground test plots (3 plots of 80 x 40 feet with 16 subplots of 20 x 10 feet; <1% slope) of silty clay loam soil (20% sand, 48% silt, 32% clay, 3.1% organic matter, pH 6.9, CEC 19.1 meq/100 g); SAN 835H was applied as SAN 836H (the sodium salt of SAN 835H). A control plot, similar in size (unspecified dimensions) to the treated plots, was located 50 feet from the treated plots. The application rate was not verified by soil monitoring pads or other valid means; however, based on the theoretical value (0.178 ppm) reported by the registrant (report p. 18), the parent compound was present at 89% (day 0) of the expected soil concentration in the 0- to 10-cm depth. Precipitation was supplemented with irrigation; total water input via precipitation and irrigation was 90% (reviewer

calculated) of the 10-year historical precipitation average for the months of June through December (Table 4; see Comment #13). A five-year plot history indicated no prior use of diflufenzopyr (Table 2). The test plot was treated during the in-life phase of the test with Roundup (glyphosate) twice and Dual (metolachlor) plus Sencor (metribuzin) once (Table 3). The depth to the water table (seasonal high) was 86 feet. Environmental data were collected onsite for the months of June through December 1995 (Table 4; see Comment #13). Daily air and soil temperatures, humidity, precipitation and irrigation throughout the study were reported in the field study notebook (p. 13); daily data were not submitted. Pan evaporation data were not reported.

Soil cores were collected seventeen days prior to application and at 0, 1, 2, 4, 7, 14, 29, 44, 61, 89, 119, 176, 363 and 506 days posttreatment; control plot samples were collected prior to application and at 0, 7, 29, 61, 119, 363 and 506 days posttreatment. At each sampling interval, eight soil cores were removed from each plot as previously described for the Ohio site. All samples were placed in a freezer (≤0 °F) within three hours of collection. Samples were transported frozen by refrigerated carrier to the analytical laboratory; samples collected prior to treatment were transported by "common carrier." Soil cores were sectioned into 10-cm depth increments and composited by subplot and depth.

Diflufenzopyr and the degradate M1 {8-methylpyrido[2,3-d]pyridazin-5(6H)-one} were extracted and analyzed as described previously for samples collected from the Ohio site (Appendix III). The limits of detection for diflufenzopyr and M1 were 0.010 ppm and 0.005 ppm, respectively. At least one control plot sample and one fortified sample were analyzed concurrently with each set of samples.

No analyses were conducted for two diflufenzopyr degradates, M5 and M9, which identified as major environmental degradates in the soil aerobic metabolism laboratory study (MRID 44170153).

Concurrent recoveries for 0- to 10-cm depth samples fortified separately at 0.01-0.1 ppm with diflufenzopyr and the degradate M1 were 35-107% and 72-107%, respectively (Tables 12-13); recoveries from the 10- to 20-cm and 20- to 30-cm depths were also reported.

In a previous study (MRID 44329606), diflufenzopyr and M1 were determined to be stable in frozen storage for up to 317 days (see Comment #2); data were not reported. Study samples analyzed for diflufenzopyr and M1 were placed in frozen storage for less than 10 months (Tables 10-11,see Comment #12). Storage stability data were not for submitted for the silty clay loam soil.

Validation of Analytical Method (MRID 44307420)

A separate method validation study (BASF Reg. Doc. No. 97/5142) for diflufenzopyr and its degradates phthalazinone (M1) and carbamoyl phthalazinone (M5) was submitted by the registrant. However, the analytical method was not the same method utilized in the four field dissipation studies reviewed in this DER (see Comment #3). Untreated soil samples were collected from a silt loam soil plot located at Leuggern, Switzerland and subsamples (50 g) were fortified with diflufenzopyr and M1 at 0.01 and 0.1 ppm, and with M5 at 0.1 ppm (report p. 8). Fortified subsamples along with Clarcel (filtration agent) were placed into screw-cap bottles. The subsamples were extracted by shaking with 0.5% sodium hydrogenocarbonate solution:acetone (1:3, v:v) followed by filtration. The subsamples were further extracted with acetone followed by filtration. The combined extracts were diluted with acetone. An aliquot of the extract was concentrated to remove the acetone, acidified and purified by solid phase extraction (SPE; Extralut column); analytes were eluted with ethyl acetate. The extract was evaporated to dryness, reconstituted in 0.5% sodium hydrogenocarbonate solution and purified by SPE (C18 column); analytes were eluted with acetonitrile:water (2:8, v:v) prior to analysis for diflufenzopyr by HPLC (Hypersil BDS-C18 column) with a mobile phase gradient of acetonitrile:0.5% trifluoroacetic acid solution (10:90 to 50:50 to 80:20, v:v) and with UV (240 nm) and diode-array detection. To analyze for phthalazinone (M1), an aliquot of the extract was concentrated to remove acetone and purified by SPE (Extrelut column); analytes were eluted with ethyl acetate. The extract was evaporated to dryness, reconstituted in water and purified by SPE (Envi-Carb column); analytes were eluted with methanol:dichloromethane (2:8, v:v) prior to analysis by GC/MS (HP-5 MS column) with SIM (single ion monitoring mass 161) detection. *Carbamoyl phthalazinone (M5) was converted to phthalazinone (M1) during the analytical procedure and was, therefore, detected as phthalazinone.* The limit of quantitation was 0.01 mg/kg for both analyses. Recoveries of samples fortified (0.01-0.1 ppm) with diflufenzopyr and phthalazinone (M1) were 52.5-105.5% (two of the ten recoveries were outside the acceptable range of 70-120%) for phthalazinone and 73.7-107.8% for diflufenzopyr (Table 2). Recoveries of samples fortified (0.1 ppm) with carbamoyl phthalazinone (M5) were 89.2-107.5% (Table 3). Additional recoveries of samples fortified (0.1 ppm) with diflufenzopyr were 76.8-89.9% (Table 4). This validation study did not include a method for identifying and quantifying the major degradates M9 (2-Keto M1) and M5.

DATA SUMMARY

New Holland, Ohio (44329605)

Diflufenzopyr (WP; 86% a.i.), broadcast applied once at a nominal rate of 0.2 lb a.i./A to bare ground plots of silt loam soil near New Holland, Ohio, dissipated with a registrant-calculated half-life of 5.2 days (unspecified r^2 value; report p. 19). Half-life calculations were based on nonlinear first order regression analysis. Diflufenzopyr was initially present in the 0- to 10-cm (top) depth at 0.090 ppm (day 0), decreased to 0.041 ppm by 4

days posttreatment and was not detected by 32 days posttreatment (Table 7). The parent compound was not present in the 10- to 20-cm depth and was detected once in the 20- to 30-cm depth at 0.016 ppm at 14 days posttreatment (Tables 8-9; see Comment #14). The degradate M1 was not detected in the soil samples. Only the soils collected at the sampling intervals beyond 32 days posttreatment (0- to 20-cm depth) and 88 days posttreatment (20- to 30-cm depth) were analyzed for the degradate M9 (see Comments #4 and 5). The degradate M9 was not detected in the soil at these sampling intervals. The degradate M5, which was identified as a major degradate in the soil aerobic metabolism study (MRID 44170153) was not assayed for in this study.

Noblesville, Indiana (44329606)

Diflufenzopyr (WP; 86% a.i.), broadcast applied once at a nominal rate of 0.2 lb a.i./A to bare ground plots of loam soil near Noblesville, Indiana, dissipated with a registrant-calculated half-life of 3.5 days (unspecified r^2 value; report p. 21). Greater than 50% of the parent compound degraded between the 2 and 4 days posttreatment (consecutive) sampling intervals. Half-life calculations were based on nonlinear first order regression analysis. Diflufenzopyr was initially present in the 0- to 10-cm depth at 0.131 ppm (day 0), increased to a maximum of 0.133 ppm by 1 day posttreatment, decreased to 0.046 ppm by 4 days posttreatment and was not detected by 29 days posttreatment (Table 7). The parent compound was not present below the 10-cm depth (Tables 8-9). The degradate M1 was not detected in the soil samples. Only soils collected at the sampling intervals beyond 29 days posttreatment were analyzed for the degradate M9 (see Comments #4 and 6). The degradate M9 was initially present in the 0- to 10-cm depth at 0.011 ppm at 60 days posttreatment, increased to a maximum of 0.019 ppm by 361 days posttreatment and decreased to 0.012 ppm by 514 days posttreatment. The degradate M9 was not observed below the 10-cm depth. This study also did not include analyses of samples for the major aerobic soil degradate M5.

Vacaville, California (44307411)

Diflufenzopyr (WP; 86% a.i.), broadcast applied once at a nominal rate of 0.2 lb a.i./A to bare ground plots of sandy loam soil near Vacaville, California, dissipated with a registrant-calculated half-life of 6.1 days (unspecified r^2 value; report p. 20). Half-life calculations were based on nonlinear first order regression analysis (see Comment #20). Diflufenzopyr was initially present in the 0- to 10-cm depth at 0.051 ppm (day 0), decreased to 0.022 ppm by 7 days posttreatment, increased to 0.035 ppm by 14 days posttreatment and was not detected by 29 days posttreatment (Table 7). The parent compound was not detected below the 10-cm depth (Tables 8-9). The degradate M1 was detected in the 0- to 10-cm depth at 0.011-0.017 ppm at 29-88 days posttreatment; the degradate was not present below the 10-cm depth. Only soils collected at the sampling intervals beyond 29 days posttreatment (0- to 20-cm depth) and 61 days posttreatment (20- to 30-cm depth) were analyzed for the degradate M9 (see Comments #4 and 19).

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The degradate M9 was detected in the 0- to 10-cm depth at 0.010-0.012 ppm at 355-596 days posttreatment; the degradate was not observed below the 10-cm depth. This study also did not include analyses of samples for the major aerobic soil degradate M5.

York, Nebraska (44307412)

Diflufenzopyr (WP; 86% a.i.), broadcast applied once at a nominal rate of 0.2 lb a.i./A to bare ground plots of silty clay loam soil near York, Nebraska, dissipated with a registrant-calculated half-life of 3.3 days (unspecified r^2 value; report p. 18). Half-life calculations were based on nonlinear first order regression analysis. Diflufenzopyr was initially present in the 0- to 10-cm depth at 0.159 ppm (day 0), decreased to 0.089 ppm by 1 day posttreatment and 0.044 ppm by 7 days posttreatment, and was not detected by 29 days posttreatment (Table 7). The parent compound was not present in the 10- to 20-cm depth and was detected once in the 20- to 30-cm depth at 0.011 ppm at 4 days posttreatment (Tables 8-9; see Comment #15).

No analyses were conducted for two of the major diflufenzopyr degradates, M5 and M9, identified in the soil aerobic metabolism laboratory study (MRID 44170153). M5 and M9 respectively attained maximum concentrations of 20% (day 14 posttreatment)and 28% (day 179) of the applied in the laboratory study, and are thus very important environmental degradates to track in any field study.

COMMENTS

1. The studies were done with technical diflufenzopyr rather than the formulated end-use product.

2. Storage stability studies were not performed using soils from the Ohio, California and Nebraska test sites. The study authors indicated that the compounds were stable in storage based on the data from a fortified field sample storage study from the Indiana study (as indicated by report 414208-4; MRID 44329606). It is required that storage stability studies be conducted using soils collected from the test sites that have been fortified separately with the parent compound and its degradates.

3. An inadequate method validation study (MRID 44307420) was submitted by the registrant. The analytical method which was submitted for validation was not the same method utilized in the four field dissipation studies. In addition, a foreign silt loam soil (from Switzerland) was utilized rather than the soils from the test sites. In the submitted method validation study, M5 was converted to phthalazinone (M1) during the analytical procedure and was detected as phthalazinone. Therefore, M5 could not be quantified in samples using this method. Furthermore, the major degradate M9, was not included in the method validation study. M5 and M9 were determined to be major degradates of

diflufenzopyr in the soil aerobic metabolism laboratory study (MRID 44170153). M5 and M9 respectively attained maximum concentrations of 20% (day 14 posttreatment)and 28% (day 179) of the applied in the laboratory study, and are thus very important environmental degradates to track in any field study.

4. The monitoring did not adequately analyze for all major degradates identified in the soil aerobic metabolism study (MRID 44170153). In the laboratory study the major degradate of SAN 835H were M1, M5 and M9. In the field dissipation studies, no samples were analyzed for M5. Samples were not analyzed for M9 until nearly a month into the field study in Ohio, Indiana and California, despite the indication that the parent was dissipating rapidly (registrant-calculated half-lives of less than 7 days). Specifically, in the Ohio study, the soil cores were first analyzed for the degradate M9 at 32 (0- to 20-cm depth) and 88 days (20- to 30-cm depth) posttreatment (Tables 7-9). In the Indiana study, the soil cores were first analyzed for the degradate M9 at 29 days posttreatment (Tables 7-9). In the California study, the soil cores were first analyzed for the degradate M9 at 29 (0- to 20-cm depth) and 61 days (20- to 30-cm depth) posttreatment (Tables 7-9). The degradate was detected in the Indiana and California bare ground studies. The study author(s) did not state why the samples collected at previous sampling intervals were not analyzed. No samples were analyzed for the major degradate M9 in the Nebraska study.

5. In the Ohio study (MRID 44329605), the reviewer noted that the parent compound completely degraded by 32 days posttreatment; however, degradates did not accumulate. The two degradates (M1 and M9), identified by the registrant, were not detected in the soil (Tables 7-9). Runoff would not a have caused the poor recoveries. The first rainfall occurred two days following application and the slope of the test plot was approximately 1% (pp. 13-14). Therefore, poor recoveries may have been due to inadequate analytical methods and storage instability (M9 only).

6. In the Indiana study (MRID 44329606), the reviewer noted that the parent compound completely degraded by 29 days posttreatment; however, the degradates did not accumulate. The degradate M1 was not detected in the soil (Tables 7-9). The degradate M9 was present in the 0- to 10-cm depth at 0.011-0.019 ppm at 60-514 days posttreatment and was not detected below the 10-cm depth. Runoff would not a have caused the poor recoveries. The first rainfall occurred two days following application and the slope of the test plot was 1% (pp. 13-14). Therefore, poor recoveries may have been due to inadequate analytical methods and storage instability (M9 only).

7. In the Nebraska study (MRID 44307412), the reviewer noted that the parent compound completely degraded by 29 days posttreatment; however, the degradate did not accumulate. The degradate M1 was present in the 0- to 10-cm depth at 0.013-0.014 ppm at 29-44 days posttreatment and was not detected below the 10-cm depth (Tables 7-9). Runoff would not a have caused the poor recoveries. The first rainfall occurred one day following application and the slope of the test plot was <1% (pp. 12-13). Therefore, poor

recoveries may have been due to inadequate analytical methods and storage instability. The analytical method did not include analysis for the degradate M9.

8. At all four of the test sites, the test compound was not applied according to the specified application method. The study author(s) stated that the anticipated maximum label rate for the test compound was two applications of 0.1 lb. a.i./A (pp. 9-10). However, the compound was applied once at a rate of 0.2 lb. a.i./A.

9. The half-lives of the parent compound in the four studies were calculated using a nonlinear first order regression analysis (SAS NLIN). The reviewer notes, however, that half-life calculations were made using residue data not corrected for soil moisture content. All residue concentrations should be calculated using the dry weight of the soil sample. Because environmental conditions during a field study may vary greatly with time, soil moisture contents at sample collection may also be highly variable. The use of moist soil weights is invalid, as the calculation of data on a moist-weight basis serves to decrease the apparent concentration of residues; the use of moist-weight data in half-life calculations is also incorrect. It is noted that in each study, the study author(s) stated that statistical analysis demonstrated that the residual sum of squares (indicative of the fit of the data to the curve) was similar for the uncorrected (moist soil weight) and corrected (dry soil weight) data sets.

10. The studies were conducted at four bare ground sites using a wettable powder (reported as SP) formulation in partial concordance with EPA data requirements on the terrestrial dissipation of diflufenzopyr.

11. In the Indiana study (MRID 44329606), sampling intervals were inadequate to accurately establish the half-life of diflufenzopyr on bare soil. Greater than 50% (0.109 ppm to 0.046 ppm) of the parent compound in the 0- to 10-cm depth degraded between 2 and 4 days (the next sampling interval) posttreatment (Table 7).

12. In each of the four studies, the study author(s) stated that the freezer temperatures were generally below 10 of and that temporary temperature spikes due to open doors, cleaning, defrosting or mechanical failure were recorded (pp. 14-16); complete temperature data were not reported. In the one freezer (1154A), temperatures reached 38 of (10 hours), 19 of (36 hours), 15 of (≤1 hour), 18 of (≤1 hour) and 16 of (≤1 hour). In the second freezer (1144A), temperatures reached 20 of, 18 of, 17 of and 18 of for an hour or less each time. The study author(s) stated that the samples remained frozen throughout all "temperature excursions" (pp. 15-16).

13. Environmental data were not reported for the duration of the studies. In the Ohio, Indiana, California (MRID 44307411), and Nebraska studies, data were submitted for the months of June or July (California site only) through December 1995 (Table 4 in each study). However, samples were collected for up to 543 (December 16, 1996), 514

(November 14, 1996), 596 (February 21, 1997) and 506 days (November 9, 1996), respectively. In the Nebraska study, the study authors stated that the total rainfall plus irrigation was about 8 inches less than the 10-year precipitation average for the site during the life of the study (p. 13).

14. In the Ohio study, the parent compound was detected once below the 10-cm depth at 0.016 ppm at 14 days posttreatment (20- to 30-cm depth; Table 9). The study author stated that the concurrently run fortified samples had residue levels of 0.008 ppm and that the detection of diflufenzopyr in these samples was believed to be due to the high background interference (p. 19).

15. In the Nebraska study, the parent compound was detected once below the 10-cm depth at 0.011 ppm at 4 days posttreatment (20- to 30-cm depth; Table 9, p. 31). The study authors stated that the detection of diflufenzopyr in this sample was believed to be due to contamination (p. 18).

16. In the Ohio study, the study author stated that the soil survey lists a seasonal high water depth of 1 to 1.5 feet; however, during soil sampling the water table was not encountered (p. 13).

17. In the Indiana study, the study authors stated that the temperature data were collected offsite (Indianapolis) for short periods of time when the onsite system was not working (p. 15).

18. In the Indiana study, the study authors stated that an old clay tile subsurface drainage system existed on the research farm, but it was not known whether the drainage was under the trial plots (p. 13).

19. In the California Study, the parent compound was initially (day 0) present at 27% of the expected soil concentration (0.187 ppm) in the 0- to 10-cm depth. The study author stated that a contributing factor to the low recovery may be that the soil moisture at the time of application was significantly different than the soil moisture at the time the sample was taken for soil analysis and that this would result in a different bulk density which would affect the theoretical residue calculation (p. 20).

20. In the California study, the corrected dissipation curve of diflufenzopyr (Figure 27, p. 78) was plotted after removing two data points that were considered to be outlying points (p. 20).

21. The formulation was reported as 86SP (pp. 11 (Nebraska), 12). The reviewer assumed that the 86SP referred to a soluble powder formulation which was reported as wettable powder by the reviewer (in the absence of a formulation code for "SP").

22. All sediment concentrations reported were corrected for moisture content by the registrant; uncorrected data were submitted, but not reported by the reviewer. The reviewer notes, however, that registrant half-life calculations were made using residue data not corrected for soil moisture content (See Comment #9).

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