

US EPA ARCHIVE DOCUMENT

3-18-99

DATA EVALUATION RECORD

STUDY 5b

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CHEM 005108                      Diflufenzopyr (SAN 1269H)                      §164-1  
CAS No. 109293-97-2  
FORMULATION--06--WETTABLE POWDER

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STUDY ID 44373708

Greenhalgh, R. 1997. SAN 1269H field soil dissipation study. Study No. BAS 97143. BASF Reg. Doc. No. 97/5323. Unpublished study performed by Ecologistics Limited, Lucan, Ontario, CANADA (in-life phase) and Xenos Laboratories, Inc., Ottawa, Ontario, CANADA (analytical phase); and submitted by BASF Corporation, Research Triangle Park, NC.

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DIRECT REVIEW TIME = 47 Hours

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## CONCLUSIONS

### Field Dissipation - Terrestrial

1. This study is partially acceptable and can be upgraded if the registrant submits additional storage stability and meteorological data. This study provides useful information on the terrestrial field dissipation of diflufenzopyr as SAN 1269H (combined with dicamba; corn label use pattern) in a bare ground plot in Ontario, Canada.
2. SAN 1269H (20.2% SAN 836H, 50.9% Dicamba) was broadcast applied at a nominal rate of 0.4 kg a.i./ha to bare ground plots of Brantford silty clay loam soil near Strathroy, Ontario. SAN 835H dissipated with a registrant-calculated half-life of 3.78 days (based on nonlinear first order regression analysis). SAN 835H was initially present in the 0- to 15-cm (top) depth at 0.029 ppm (day 0), decreased to 0.018 ppm by 1 day posttreatment and was not detected by 14 days posttreatment. The test compound was not detected below the 15-cm depth. The minor degradate M1 was present in the 0- to 15-cm depth at a maximum of 0.006 ppm at 14-29 days posttreatment and was not detected below the 15-cm depth. The expected degradate M9 was not detected at any sampling interval at any depth. This field study did not monitor for M5, a major metabolite in the laboratory aerobic soil metabolism study (MRID 44170153).

## METHODOLOGY

SAN 1269H (70 WG 403 DP; 20.2% SAN 836H, 50.9% Dicamba) was broadcast applied (boom sprayer equipped with eight flat fan nozzles; p. 12) as a spray at a nominal rate of 0.4 kg a.i./ha onto bare ground plots (20 x 8 m with 100 subplots of 2 x 0.75 m; ~1% slope, p. 10) of Brantford silty clay loam soil (13.1% sand, 48.8% silt, 38.1% clay, 1.47% organic carbon, pH 7.3, CEC 26.9 cmol+/kg; p. 11) in Ontario, Canada; SAN 1269H was applied as a mixture of SAN 836H (the sodium salt of SAN 835H) and Dicamba (p. 9). A control plot, similar in size (unspecified dimensions) to the treated plots, was located 16 meters from the treated plots (p. 11). The application rate was not verified by soil monitoring pads or other valid means. The test plots were not irrigated (p. 12); the total percentage of water input via precipitation based on the historical precipitation average could not be determined (see Comment #10). Total precipitation for the months of June through October 1996 was 458.1 mm (Table 2, p. 20). A three-year plot history indicated no prior use of SAN 1269H (Table 1, p. 20; see Comment #11). The test plot was treated once during the study period with Roundup (glyphosate). The depth to the water table was approximately 8 meters (p. 10). Environmental data were collected onsite for the months of June through October 1996 and May 1997 (Table 2, p. 20; see Comments #2 and #9). Pan evaporation data were not reported.

Soils were sampled one day prior to application and at 0, 1, 2, 4, 7, 14, 29, 44, 61, 92, 125

and 330 or 331 days posttreatment (p. 13); control plot samples were collected one day prior to application and at 29, 125 and 331 days posttreatment. Twenty soil cores were randomly collected per plot in two phases; an acetate sleeve-lined, manually operated Concord soil probe (0- to 15-cm depth) and an acetate sleeve-lined Concord hydraulic soil probe mounted on a tractor were used to collect a 0- to 15-cm depth sample (6.35-cm i.d.) and a 15- to 90-cm depth sample (3.18-cm i.d.; p. 13). Pretreatment and 0 day posttreatment samples were only collected to a depth of 15 cm. All samples were placed in a freezer ( $\leq -15$  °C) within six hours of collection. Samples were transported frozen on dry ice to the analytical laboratory. Soil cores were sectioned into 15-cm depth increments and composited by subplot and depth (p. 14).

SAN 835H {2-(methyl-([3,5-difluorophenylamino]carbonyl)-hydrozono)methyl-3-pyridinecarboxylic acid} and the degradate M1 {8-methylpyrido[2,3-d]pyridazin-5(6H)-one} were extracted from the soil samples by shaking with 0.5% NaHCO<sub>3</sub> in water and acetone (unspecified volume ratio) followed by centrifugation and filtration (p. 14; Appendix II, p. 110-111). The acetone was evaporated and the remaining basic aqueous portion was partitioned with dichloromethane. The organic phase containing M1 was evaporated, redissolved in toluene and passed through a SPE (Si-60) cartridge. Compounds were eluted from the column with 12% acetone in toluene. The eluate was evaporated to near dryness and redissolved in toluene prior to analysis by GC (RTX-5-Amin column) with thermionic specific detection (TSD); the limit of quantitation was 0.002 ppm. The aqueous layer was acidified (formic acid) to convert SAN 835H to M1, partitioned with dichloromethane, and analyzed as stated above; the limit of quantitation for SAN 835H was 0.005 ppm. A correction factor was used to determine SAN 835H residues detected as M1 (p. 110). The degradate M9 {8-methylpyrido[2,3-d]pyridazine-2,5(1H,6H)-dione} was extracted from the soil samples by shaking twice with methanol:1% aqueous acetic acid (3:1, v:v) followed by centrifugation and filtration (pp. 14-15; Appendix II, p. 111). The combined extracts were concentrated, redissolved in deionized water and filtered (0.45  $\mu$ ) prior to analysis by HPLC (Lichrosorb RP-18 column) with a mobile phase of 0.1% trifluoroacetic acid in water:0.1% trifluoroacetic acid in acetonitrile (95:5, v:v) and UV (240 nm) detection; the limit of quantitation was 0.01 ppm.

Concurrent recoveries for samples fortified with SAN 835H (0.01-0.1 ppm) and the degradates M1 (0.002-0.1 ppm) and M9 (0.01-0.1 ppm) were 70.4-85.5%, 72.1-107% and 74.0-84.3%, respectively (pp. 14-15; Table 6, p. 27). Only sets of samples with recoveries between 70-120% were considered valid.

In a previous study (MRID 44329606), SAN 835H and M1 were determined to be stable in frozen storage for up to 317 days in an unidentified soil (p. 13; see Comment #1); data were not reported. Study samples analyzed for SAN 835H and M1 were stored up to 329 days prior to analysis (Table 3, pp. 21-24). Storage stability data for the degradate M9 were not submitted. Storage stability data were not submitted for the parent compound

and its degradates in the test soil.

In a method validation study, recoveries from soil samples fortified with SAN 835H at 0.002-0.200 ppm and with M1 at 0.005-0.200 ppm were 84.8-108% (with the exception of one recovery of 130%) and 74.0-117%, respectively (Appendix II, Table IIA, p. 122). Recoveries from soil samples fortified with M9 at 0.010-0.100 ppm, were 70.7-75.5% (Appendix II, Table IIB, p. 123).

#### DATA SUMMARY

SAN 1269H (20.2% SAN 836H, 50.9% Dicamba) was broadcast applied at a nominal rate of 0.4 kg a.i./ha to bare ground plots of Brantford silty clay loam soil near Strathroy, Ontario. SAN 835H dissipated with a registrant-calculated half-life of 3.78 days (unspecified  $r^2$  value; p. 18). The half-life calculation was based on nonlinear first order regression analysis and nonadjusted residue data (p. 15; see Comment #13). SAN 835H was initially present in the 0- to 15-cm (top) depth at 0.029 ppm (day 0), decreased to 0.018 ppm by 1 day posttreatment and was not detected by 14 days posttreatment (Table 4, p. 25). The test compound was not detected below the 15-cm depth (Tables 8-9, pp. 29-30). The minor degradate M1 was initially present in the 0- to 15-cm depth at 0.002 ppm at 1 day posttreatment, increased to a maximum of 0.006 ppm by 14-29 days posttreatment and was not detected by 331 days posttreatment (Table 4, p. 25); M1 was not detected below the 15-cm depth (Tables 8-9, pp. 29-30). The expected degradate M9 was not detected at any sampling interval at any depth (Tables 10-11, pp. 31-32).

#### COMMENTS

1. A storage stability study was not performed using soil from the Ontario test site. The study authors indicated that SAN 835H and M1 were stable in storage based on the data submitted on the terrestrial field dissipation of SAN 835H in Indiana loam soil (MRID 44329606). The storage stability of the degradate M9 was not studied. 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 expected degradates and stored for a duration equal to the longest storage interval for the test samples.
2. Incomplete meteorological conditions were reported. Daily meteorological conditions were not reported. The monthly maximum and minimum temperatures and the total precipitation were reported for only six months (June to October 1996 and May 1997) of the 11-month study. The study author stated that meteorological data were included in the field study notebook (p. 12); however, data were not submitted.
3. This field study did not monitor for M5, a major metabolite in the laboratory aerobic soil

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metabolism study (MRID 44170153). In the laboratory study with phenyl-labeled diflufenzopyr, M5 attained a maximum concentration of 19.5% of the applied 14 days posttreatment. In the laboratory study with pyridinyl-labeled diflufenzopyr, M5 attained a maximum concentration of 17.9% of the applied 30 days posttreatment. M5 declined to less than 3% of the applied by 360 days posttreatment in both labels.

4. The study authors noted that this study does not meet U.S. Good Laboratory Practices and Standards due to several reasons:
  - i.) Soil characteristics, weather data, field site history, and some site management data were not collected under GLP, but were believed to be adequate.
  - ii.) The uniformity and stability of the test substance was not determined prior to the experiment start date or during the study, but that testing of the uniformity and stability "is in progress, and does not affect the conclusions of the study."
  - iii.) The field portion of the study was not conducted according to GLP.
  - iv.) The HPLC standards had exceeded their expiration dates for the last four injected sets, injected between June 13-18, 1997. The report stated that "this did not affect the results of the study."
5. The reviewer noted that SAN 835H completely degraded by 14 days posttreatment; however, only a single degradate was observed at or near the limit of detection. The minor degradate M1 was present in the 0- to 15-cm depth at 0.002-0.006 ppm at 1-125 days posttreatment (Table 4, p. 25) and was not detected below the 15-cm depth (Tables 8, 9; pp. 29, 30). The degradate M9 was not detected in the soil (Tables 10, 11; pp. 31, 32). It is not likely that runoff would have caused the poor recoveries, as the first rainfall occurred six days following application and the slope of the test plot was 1% (pp. 11, 13). The reviewer notes that the poor recoveries may have been due to inadequate analytical methods and storage instability.
6. It was unclear to the reviewer whether the pesticide was applied at the maximum label rate. The registrant stated that the maximum label rate for use in Canada was 0.4 kg a.i./ha (p. 8). However, it was unclear whether the active ingredient referred to was SAN 836H or SAN 836H plus dicamba. The theoretical pesticide concentration (reviewer calculated) in the 0- to 15-cm depth would be 0.194 ppm if the a.i. referred to was SAN 836H only, and 0.054 ppm if the a.i. referred to was SAN 836H plus dicamba (i.e., SAN 1269H). The reviewer notes that the day 0 concentration in the 0- to 15-cm depth was 0.29 ppm (Table 4, p.25), indicating that the active ingredient referred to in the maximum label rate was SAN 836H (or SAN 835H) and did not include dicamba.
7. The study was conducted at a bare ground site and submitted in partial fulfillment of EPA data requirements on the terrestrial dissipation of diflufenzopyr as SAN 1269H. The study author stated that the study was intended to meet the Canadian requirement T-1-255 for the registration of new pesticides as defined by the Pest Management Regulatory Agency (p. 1).

8. The study author stated that the frozen storage temperatures were generally below  $-15^{\circ}\text{C}$  and that temporary temperature spikes were recorded due to open doors, cleaning and defrosting (p. 13); temperature data were not reported.
9. The study author stated that some of the environmental data were collected offsite, from the Environmental Canada weather station near Nairn about 9 km north-east of the test site (p. 12).
10. The historical precipitation average for the test site was not reported; therefore, the total percentage of water input via precipitation based on the historical precipitation average could not be determined. The study author stated that the monthly rainfall was below average for the month of August and above average for the month of September (p. 12).
11. The reviewer noted that the previous pesticide history for the site included application of dicamba (Banvel; Table 1, p. 20). Dicamba was present in the test formulation (SAN 1269H: 20.2% SAN 836H, 50.9% Dicamba); however, samples were only analyzed for SAN 835H and its degradates.
12. The formulation was reported as SAN 1269H 70 WG 403 DP (p. 10). The reviewer assumed that the 70 WG indicated a wettable granule formulation (for SAN 836H); this was recorded in this DER as wettable powder (formulation 06) by the reviewer in the absence of a formulation code for wettable granule.
13. The study author stated that the half-life (3.78 days) was calculated using "nonadjusted" data points (p. 15; p. 116; Figure 19, p. 51). Based on the last footnote to Table 4 (p. 25), the reviewer assumed that the "nonadjusted data points" represented residue concentrations determined prior to corrections for 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. For example, at day 0, the parent compound was detected at 0.029 ppm based on adjusted (dry-weight basis) data; using moist-weight data, the parent was observed at only 0.022 ppm. The registrant-calculated half-life should be recalculated using dry-weight data.
14. It could not be determined whether the soil texture (silty clay loam) was characterized using the USDA classification system.
15. All concentrations reported herein were corrected for moisture content by the registrant; uncorrected data were submitted, but not reported by the reviewer.

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