Soil Photolysis of Pymetrozine

Report: Sparrow, K. 2000. Photodegradation of ^{14}C-triazinyl-6-CGA-215944 on soil surface under artificial light. Laboratory ID. 544-00. Unpublished study performed and submitted by Novartis Crop Protection, Inc. Greensboro, NC.

Document No.: MRID 45208702

Guideline: OPPTS 835.2410

Statements: Good Laboratory Practice (GLP) Compliance and Quality Assurance statements were provided with the study (pp. 3, 5).

Classification: This study is classified as **Supplemental**. This study is scientifically valid and provides useful information on the photodegradation of pymetrozine on soil; however, the study did not employ a range of dielectric constants and a nonpolar solvent to maximize unextracted residues, which totaled 11.5-13.2% of the applied.

PC Code: 101103

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U.S. EPA Date: Date: 2018.02.08 07:57:51 -05'00'

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DATA EVALUATION RECORD

STUDY 2

PC No. 101103 Pymetrozine §161-3
CAS No. 123312-89-0
DP Barcode D270145
FORMULATION-00-ACTIVE INGREDIENT

STUDY ID 45208702
Sparrow, K. 2000. Photodegradation of ^{14}C-triazinyl-6-CGA-215944 on soil surface under artificial light. Laboratory ID. 544-00. Unpublished study performed and submitted by Novartis Crop Protection, Inc. Greensboro, NC.

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ABSTRACT

Degradation - Photodegradation on Soil

The photolysis of [^{14}C-triazinyl-6-CGA-215944]pymetrozine [1,2,4-triazin-3(2H)-one, 4,5-dihydro-6-methyl-4-[(3-pyridinylmethylene)amino]-,(E)]; radiochemical purity 98.5%], at 0.101 ppm (0.187 lbs a.i./A), was studied using sandy loam soil incubated at 75% of 0.33 bar moisture. Samples were maintained at approximately 25°C and irradiated for 12 hours/day for up to 30 days with a filtered xenon lamp. The lamp yielded an intensity of 3.01 x 10^{-3} W/cm^2 (320-400 nm) and was comparable to 1 day of North Carolina sunlight. Dark controls were also maintained at 25 ±1°C for up to 30 days. All samples were analyzed for total radioactivity using LSC, and for parent compound and its degradates by two-dimensional TLC.

The registrant-calculated DT_{50} was 18.5 days for the irradiated samples and 16.6 days for the dark controls. The pattern of degradation was similar, with pymetrozine comprising 88.60-91.06% of the applied at time 0, 78.29-81.52% at 1 day, 63.56-65.98% at 7 days, 45.97-58.07% at 22 days, and 38.09-52.53% at 30 days. In the irradiated and dark control samples, two degradates,

CGA-294849 [1,2,4-triazin-3,5(2H,4H)-dione, 4-amino-6-methyl] and

CGA-359009 [1,2,4-triazin-3(2H)-one, 4,5-dihydro-5-hydroxy-6-methyl-4-[(3-pyridinylmethylene)amino]-

were identified at maximum averages of 1.04-1.14% and 10.54-14.83% of the applied, respectively; up to nine unidentified degradates each averaged ≤1.56% of the applied. At 30 days posttreatment, unextracted [^{14}C]residues in the irradiated and dark controls were 11.55-13.2% and $^{14}CO_2$ totaled 1.73-5.85% of the applied radioactivity. Material balances (irradiated and dark soil) ranged from 96.72 to 112.32% of the applied.

MATERIALS AND METHODS

[^{14}C-Triazinyl-6-CGA-215944]pymetrozine [1,2,4-triazin-3(2H)-one, 4,5-dihydro-6-methyl-4-[(3-pyridinylmethylene)amino]-,(E)]; radiochemical purity 98.5%, specific activity 63 µCi/mg, Reference No. GAN-XL-2-; Novartis; pp. 17, 45] was dissolved in water and acetonitrile to yield a [^{14}C]pymetrozine dosing solution of 0.101 ppm (approximately 0.187 lb a.i./A; p. 21). Samples (approximately 7 g) of sieved (2 mm) sandy loam soil (62.2% sand, 34.1% silt, 3.7% clay, 0.8% organic matter, pH 7.5 (water), CEC 7.0 meq/100g; p. 62) were incubated at 75% of 0.33 bar moisture and placed in vessels (2 x 2 x 5 cm; pp. 20, 22, 37). An aliquot (70 µL) of [^{14}C]pymetrozine was added to each soil sample. The samples were vortexed, sealed with an open top cap and Teflon-coated septum, and the lid of each vial was wrapped with parafilm. The samples were set on their sides in a water bath

maintained at 25 ± 1°C, covered with a Pyrex glass plate, and placed directly under a Suntest CPS or Suntest CPS+ Photolysis Unit (Suntest Accelerated Exposure Unit, W.C. Heraeus, Hanau, Germany; p. 23). The samples were irradiated with a xenon arc lamp (1.8 kW) for 12 hours per day for up to 30 days. The lamp was equipped with a quartz glass dish with a selective reflective coating and a UV glass filter to eliminate radiation below 290 nm (p. 23; Figure 6, p. 66). The average daily intensity was approximately 7.8 x 10^{-3} W/cm^2. Natural and artificial spectral distributions (200-700 nm) were made using an International Light IL-1700 with power supply and double monochromator (p. 20). The natural sunlight spectral distribution of 300-400 nm was used to adjust the intensity of the Suntest CPS Units 1 and 4; a natural sunlight-to-artificial light ratio of 1.0 was used as an ideal state (p. 37). The ratios for Suntest 1 and 4 were 0.86-1.14 for the duration of the study. Spectral distributions of the xenon lamp and natural sunlight were comparable (Figure 4, p. 68). It was determined that 12 hours of irradiation with the xenon lamp were comparable to 1 day of North Carolina summer sunlight (p. 37; Figure 4, p. 64). The water bath temperature was monitored by an Environmental Monitoring System (EMS) with an Omega thermocouple inserted into a surrogate sample (Figure 5, p. 65). For dark controls, the sealed vessels were wrapped in aluminum foil to exclude light and incubated in a constant temperature room at 25 ± 1°C (p. 23). The constant temperature room was monitored by the EMS and was equipped with a Honeywell hydrothermograph. Each vial was equipped with inlet/outlet ports to allow for the collection of volatiles. Humidified air was continuously drawn (19 mL/minute) through each vial, then sequentially through a blank trap, an ethylene glycol trap, a blank trap, 2 potassium hydroxide traps, and a final blank trap (pp. 25-26). Duplicate irradiated and non-irradiated vessels were removed for analysis at 0, 0.5 (12 hours), 1, 3, 7, 15, 22, and 30 days posttreatment (p. 24). The samples were stored frozen at <-10°C (some samples temporarily stored at 4°C) for up to 2 months (pp. 24, 29, 42). Volatiles were collected continuously from the time of dosing until the last sampling interval for the irradiated and dark control samples (p. 39).

Soil samples were extracted twice with acetonitrile:water (80:20, v:v), shaken, and centrifuged for 10 minutes at ¾ speed (p. 26). Like extracts were combined, stored frozen, and later analyzed for total radioactivity using LSC (limit of detection 0.00008-0.0002 µg; p. 34), and two-dimensional TLC. The remaining soil was used in further extractions. Soil samples were extracted twice with acetonitrile:pH 9 water (3:1), sonicated, shaken, and centrifuged for 10 minutes at ¾ speed (p. 27). The extracts were analyzed using LSC and two-dimensional TLC using the following conditions (pp. 30-31):

Solvent system	Phase	Components	Composition (v.v:v:v)	Plate type
SS1	Normal	Chloroform:methanol:acetic acid:water	83:13:1:1	20 x 20 cm, 0.25 mm silica gel
SSII	Normal	Chloroform:methanol:ammoni	80:30:4:2	20 x 20 cm, 0.25 mm

		um hydroxide:water		silica gel

Following development, areas of radioactivity were quantified using a Fujix Bio-imaging Analyzer (p. 32). Unlabeled reference compounds were cochromatographed with the soil extracts, and following development, were visualized under UV light (254 nm).

To generate sufficient material for identification of [^{14}C]compounds, six bulk samples were dosed as described above and incubated in the dark for 15 days (p. 34). The samples were extracted twice with acetonitrile:water (80:20, v:v), shaken, and centrifuged for 10 minutes at ¾ speed. The extracts were pooled, concentrated by rotary evaporation and under a nitrogen stream, and analyzed by preparatory one-dimensional TLC using multiple TLC plates (p. 35). The radioactive bands were scraped from the TLC plates and isopropanol. The sample was sonicated for about 15 minutes, then centrifuged for 10 minutes at 3/4 speed; the extraction was repeated once. The combined supernatants were analyzed by LSC. The extraction was repeated using acetonitrile, and the acetonitrile extracts were analyzed by LSC. The extracts were analyzed by two-dimensional TLC; the final extracts were concentrated to dryness and analyzed by MS.

To separate the humin fraction from the humic acid/fulvic acid fractions, the remaining soil pellets were extracted with 0.5M sodium hydroxide, vortexed, shaken for 16 hours, centrifuged for 10 minutes, and washed twice with 0.5 M sodium hydroxide (p. 27). The supernatants were combined and analyzed by LSC. To characterize the humic acid/fulvic acid fractions, the 30-day extract was acidified (pH 1) with HCl, centrifuged for 10 minutes, and analyzed by LSC. The precipitant was dissolved in 0.1 M sodium hydroxide and analyzed by LSC. The insoluble fraction was combusted to determine the amount of humin fraction.

Unextractable [^{14}C]residues remaining in the extracted soil samples were quantified by LSC following combustion (p. 40). Aliquots of the trapping solutions were analyzed for total radioactivity by LSC.

Microbial viability analysis was conducted on days 0 and 30 (p. 38). To determine biomass, soil (25 g) was amended with a glucose/talcum (1 g) mixtures and allowed to respire until the maximum respiration had occurred (p. 20).

RESULTS/DISCUSSION

[^{14}C-Triazinyl-6-CGA-215944]pymetrozine (1,2,4-triazin-3(2H)-one, 4,5-dihydro-6-methyl-4-[(3-pyridinylmethylene)amino]-,(E)); radiochemical purity 98.5%], was studied in sandy loam soil that was treated at a rate equivalent to 0.187 lb a.i./A. [^{14}C]Pymetrozine degraded with a registrant-calculated DT_{50} of 18.5 days on sandy loam soil that was irradiated for 12 hours per day with a filtered xenon arc lamp (intensity 3.01 x 10^{-3} W/cm^2 at 320-400 nm) at 25 $\pm$ 1°C for up to 30 days (Figure

50, p. 110). The intensity of the artificial light source was determined to be comparable to 1 day of average sunlight intensity in Greensboro, North Carolina (p. 37). The dark controls degraded with a registrant-calculated DT_{50} of 16.6 days. Two degradates,

CGA-294849 [1,2,4-triazin-3,5(2H,4H)-dione, 4-amino-6-methyl] and

CGA-359009 [1,2,4-triazin-3(2H)-one, 4,5-dihydro-5-hydroxy-6-methyl-4-[(3-pyridinylmethylene)amino]-

were identified in extracts from the irradiated and dark control samples.

Irradiated samples: Pymetrozine decreased from an average of 91.06% of the applied at time 0 to 78.29% at 1 day, 63.56% at 7 days, 58.07% at 22 days, and 38.09% at 30 days posttreatment (Table 5, pp. 51-52). CGA-294849 and CGA-359009 were detected at maximum averages of 1.04% and 10.54% of the applied, respectively, at day 30. Six unidentified degradates each averaged ≤1.56% of the applied. Unextracted [^{14}C]residues were a maximum of 11.55-13.20% and $^{14}CO_2$ totaled 1.73-5.85% of the applied at 30 days posttreatment (Table 2, p. 46). Of the radioactivity in the 30-day unextracted soil, 23.08-26.03% of the applied was fulvic acid, 3.98-4.69% was humic acid, and 11.55-13.20% was humin (p. 40). Material balances ranged from 97.23 to 103.71% of the applied.

Dark controls: Pymetrozine decreased from an average of 88.60% of the applied at time 0 to 81.52% at 1 day, 65.98% at 7 days, 45.97% at 22 days, and was 52.53% at 30 days posttreatment (Table 5, pp. 53-54). CGA-294849 and CGA-359009 were detected at maximum averages of 1.14% and 14.83% of the applied, respectively, at 22 days posttreatment. Nine unidentified degradates each averaged ≤1.56% of the applied. Unextracted [^{14}C]residues and $^{14}CO_2$ were 7.83-10.47% and ≤4.02% of the applied, respectively, at 30 days posttreatment (Table 2, p. 46). Of the radioactivity in the 30-day unextracted soil, 20.97-26.23% of the applied was fulvic acid, 1.86-3.34% was humic acid, and 7.83-10.47% was humin (p. 40). Material balances ranged from 96.72 to 112.32% of the applied.

Soil microbial viability throughout the study was confirmed. The initial biomass was 161.6 mg C/kg dry soil. Plate counts decreased from 1.74 x 10^6 to 7.69 x 10^5 CFU on day 30 (p. 38).

DEFICIENCIES/DEVIATIONS

1. Soil extracts were stored frozen at <-10°C (some samples temporarily stored at 4°C) for up to 2 months prior to analysis (pp. 29, 42). TLC analysis of the 0 Hour Replicate 2 sample analyzed near study initiation and then again after approximately 2 months of frozen storage showed that no significant degradation occurred during storage (Figure 10, p. 70).

2. The study author noted that the program used to determine a DT_{50} for pymetrozine, Modelmaker®, cannot optimize when an outlier data point is present; therefore, the irradiated day 30 results were not used due to the higher percent extractable residues (p. 41). The DT_{50} for pymetrozine was determined to be 18.8 days (Figure 50, p. 110). The Dynamac reviewer determined a degradation half-life of 35.4 days (r^2 = 0.719) for pymetrozine (Attachment 2).

3. The study author calculated half-lives for pymetrozine in the dissolved phase. The half-life was 5.29 days for the irradiated samples and 5.71 days for the dark controls.

4. Subdivision N guidelines specify that the temperature should deviate no more than 1°C. The temperature on dose day dropped to 22°C for approximately 5 hours (p. 36; Figure 8, p. 68). However, the study author concluded that this deviation did not compromise the study results based on the fact that similar study results were obtained for the pyridinyl labeled soil photolysis study (p. 36).

5. The distance from the light source to the soil surface in the vial was not reported.

6. Currently, EPA considers GC/MS procedures the only means for positively identifying compounds. It is also acceptable to use two significantly different methods, such as HPLC and TLC using different stationary and mobile phases. In this study, two-dimensional TLC was the only procedure used to identify pymetrozine and its degradates.

7. The UV/visible spectrum of pymetrozine at 0.09 ppm in water was presented in Figure 3 (p. 63).

8. Similar results were obtained in a related photodegradation on soil study using [^{14}C-pyridinyl-2-CGA-215944]pymetrozine (MRID 45208701; Study 1 of this submission). In that study, pymetrozine degraded with a registrant-calculated DT_{50} of 18.8 days for the irradiated samples and 18.2 days for the dark controls. The pattern of degradation was similar, with pymetrozine comprising 97.26-98.60% of the applied at time 0, 79.76-81.31% at 1 day, 60.16- 64.51% at 7 days, 47.24-47.79% at 22 days, and 39.95-54.77% at 30 days. In the <u>irradiated and dark control samples</u>, three degradates, CGA-300407 (3-pyridinecarboxaldehyde), CGA-180777 (pyridinecarboxylic acid), and CGA-359009, were identified at maximum averages of 2.80-3.57%, 1.57-1.91%, and 8.76-9.51%, respectively; up to 11 unidentified degradates each averaged ≤5.74% of the applied. The Dynamac reviewer notes two degradates identified in that study, CGA-300407 (3-pyridinecarboxaldehyde) and CGA-180777 (pyridinecarboxylic acid) were not identified in the present study.

9. The sandy loam soil used in the study was the same soil used in an aerobic soil metabolism study (p. 17; MRID 44024966).

10. Good Laboratory Practice (GLP) Compliance and Quality Assurance statements were provided with the study (pp. 3, 5).

11. The solubility of pymetrozine in water was reported to be 0.29 g/L (p. 18).

12. The study author stated that the nominal application rate (0.09 ppm) was equivalent to the maximum recommended field use rate of 0.187 lb a.i./A. The dose rate was derived based on a soil depth of 0.5 feet, with a bulk density of 1.5 g/cm^3 (based on dry weight) and a homogeneous distribution of material throughout the soil (p. 21).

13. Unextracted residues exceeded 10% AR.