Soil Photolysis of Pymetrozine

Report: Parker, S. (1988) Development of a method to investigate the photodegradation of pesticides. Brighton Crop Protection Conference-Pest and Diseases p. 663-668.

Schulze-Aurich, J. (1995) Photolysis (5-(carbon 14))--Pyridine-Labelled CGA-215944 on Soil Surface Under Laboratory Conditions: Lab Project Number: 94SA02: 488-94: PR 94SA02. Unpublished study prepared by Ciba-Geigy Ltd. 195 p.

Schulze-Aurich, J. (1995) Photolysis (5-(carbon 14))--Triazine-Labelled CGA-215944 on Soil Surface Under Laboratory Conditions: Lab Project Number: 93MU02: 606-93: PR 50/94. Unpublished study prepared by Ciba-Geigy Ltd. 176 p.

Document No.: MRIDS 44411323, 44411324, 44411325

Guideline: OPPTS 835.2410

Classification: A study classification was not provided on the attached Data Evaluation Record; therefore, these studies are now classified as Supplemental. These studies are scientifically valid and provide 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 ranged from 45.2 - 50.1% applied radioactivity in the irradiated samples in the triazine and pyridine studies, respectively.

PC Code: 101103

Reviewer: Jessica L. O. Joyce, Fate Scientist
U.S. EPA Date: Date: 2018.02.08 07:56:57 -05'00'

Rochelle F.H. Bohaty, Senior Scientist
U.S. EPA Date: 2018.02.08 07:24:05 -05'00'

TEXT SEARCHABLE DOCUMENT 2011

DATA EVALUATION RECORD

STUDY 3

CHEM 101103 Pymetrozine §161-3
CAS No. 123312-89-0
FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 44411324
Schulze-Aurich, J. 1995. Photolysis of [5-^{14}C] - pyridine-labelled CGA-215944 on soil surface under laboratory conditions. Laboratory Project ID: 94SA02. Unpublished study performed and submitted by Ciba-Geigy, Ltd., Basel, SWITZERLAND.

STUDY ID 44411325
Schulze-Aurich, J. 1995. Photolysis of [5-^{14}C] - triazine-labelled CGA-215944 on soil surface under laboratory conditions. Laboratory Project ID: 93MU02. Unpublished study performed and submitted by Ciba-Geigy, Ltd., Basel, SWITZERLAND.

STUDY ID 44411323
Parker, S. 1988. Development of a method to investigate the photodegradation of pesticides. Published study submitted by Novartis Crop Protection, Inc., Greensboro, NC.

DIRECT REVIEW TIME = 66 hours

REVIEWED BY: M. T. Holdsworth, M.S.
Signature:
TITLE: Scientist
Date:

EDITED BY: C. A. Little, Ph.D.
Signature:
TITLE: Sr. Scientist/Asst. Project Manager Date:

APPROVED BY: P. H. Howard
Signature:
TITLE: Project Manager
Date:
ORG: Syracuse Research Corp.
Arlington, VA 22202
TEL: 703/413-9369

APPROVED and REVISED BY: Thuy L. Nguyen, MS
TITLE: Chemist
ORG: ERB III/EFED/OPP
TEL: 703/605-0562

Shaw Lane Copy

2087118

TEXT SEARCHABLE DOCUMENT 2011

SIGNATURE: EFED Share drive Copy

TEXT SEARCHABLE DOCUMENT 2011

CONCLUSIONS

Degradation - Photodegradation on Soil

1. This study does not meet Subdivision N Guidelines for the fulfillment of EPA data requirements on photodegradation on soil for the following reason:

   (i) the soil used in this study (Les Evouettes silt loam soil) was not the same type of soil used in the aerobic soil metabolism study (Hanford sandy loam soil). The soil also has high %organic matter, thus increases the chemical binding to soil and provides inaccurate information on the actual photodegradation of pymetrozine in soil.

   (ii) there is a large discrepancy between the half-life of the dark control and the half-life from the aerobic soil metabolism study.

2. This study is scientifically valid and provides useful information on the degradation of pymetrozine on soil surface, in the presence of light. However, pattern and rate of photodegradation are questionable. Supplemental data using the same soil type as in the aerobic soil metabolism study (or soil with low %OC) is needed to fulfill the EPA data requirements.

3. Pyridinyl ring-labeled [5-^{14}C]pymetrozine, at a nominal application rate of 11.2 ppm, degraded with a registrant-calculated half-life of 4.3 sunlight equivalent days (40° N) on Les Evouettes silt loam soil adjusted to 75% of 0.33 bar moisture content and incubated at 23.6 ± 0.3^{o} C for 34 days while irradiated with a xenon arc lamp (12 hours of light per day). In contrast, the parent compound degraded in dark controls with a registrant-calculated half-life of 10.4 days. Biphasic degradation was observed. The reviewer-calculated photolytic half-life was determined to be 6.22 days (at 40° N). In irradiated soils, the parent compound was initially present at 102.0% of the applied radioactivity, decreased to 53.0% by 3 days posttreatment and was 8.4% of the applied at 34 days. In contrast, the parent in dark controls was initially present at 102.0% of the applied radioactivity, decreased to 59.1% by 7 days posttreatment and was 24.5% of the applied at 34 days. The major degradate M2 was a maximum of 28.6% of the applied at 7 days and was 9.1% at 34 days. In contrast, M2 in dark controls increased throughout the incubation period to a maximum of 46.6% of the applied radioactivity by 34 days posttreatment. The minor degradate M4 was maximums of 5.9% (day 34) and 7.6% (day 15) of the applied radioactivity in the irradiated and dark control samples, respectively. Nonextractable [^{14}C]residues were maximums of 50.1% of the applied radioactivity in irradiated samples and 15.7% in dark control samples at 34 days. Radiolabeled $^{14}CO_2$ accounted for 25.8% and 6.0% of the applied radioactivity at 34 days posttreatment for the irradiated and dark controls, respectively.

   Triazine ring-labeled [6-^{14}C]pymetrozine, at a nominal application rate of 43.8 ppm, degraded with a registrant-calculated half-life of 1.6 sunlight equivalent days (40° N) on Les Evouettes silt loam soil adjusted to 75% of 0.33 bar moisture content and incubated at 23.5 ± 0.6^{o} C for 34 days while irradiated with a xenon arc lamp (12 hours of light per day).

TEXT SEARCHABLE DOCUMENT 2011

In contrast, the parent compound degraded in dark controls with a registrant-calculated half-life of 5.9 days. Biphasic degradation was observed. The reviewer-calculated photolytic half-life was determined to be 4.4 days (at 40° N). In irradiated soils, the parent compound was initially present at 101.8% of the applied radioactivity, decreased to 61.3% by 1 day posttreatment and was 7.6% of the applied at 32 days. In contrast, the parent in dark controls was initially present at 97.4% of the applied radioactivity, decreased to 50.3% by 7 days posttreatment and was 24.8% of the applied at 32 days. The major degradate M3 was a maximum of 33.5% of the applied at 3 days and was 7.4% at 32 days. In contrast, M3 in dark controls was a maximum of 55.0% of the applied radioactivity at 16 days posttreatment. The minor degradate M5 was a maximum of 5.4% (day 16) and 5.7% (day 32) of the applied radioactivity for the irradiated and dark control samples, respectively. Nonextractable [^{14}C]residues were maximums of 45.2% of the applied radioactivity in irradiated samples and 18.5% in dark control samples at 32 days. Radiolabeled $^{14}CO_2$ accounted for 22.2% and 2.1% of the applied radioactivity at 32 days posttreatment for the irradiated and dark controls, respectively.

Based on the reported rate of formation and decline of the degradates between the irradiated and the dark control samples, it is apparent that pymetrozine underwent some photolytic degradation on the surface of the tested soil. However the short half-life of the dark control samples (net registrant-calculated half life of ≤10.4 days) contradicts the long aerobic soil metabolism half life (_300 days). Note that there are excessive uncharacterized non-extractable radioactivity in both the irradiated (25%) and non-irradiated (50%) samples. A review of the adsorption/desorption studies indicate pymetrozine has high affinity to soils (K_d ranging from 3.1 to 23.3 mL/g), especially soil with high organic carbon content. Therefore, it is very likely that these uncharacterized radioactivity could be bound residues of the parent pymetrozine, and the short half lives could misrepresent the rate of degradation of pymetrozine in soils. Photolysis in soil should be performed on lower organic content (such as the soil used in the aerobic metabolism studies) in order to minimize soil binding effect and better characterize the rate of degradation of this chemical on soil surface under irradiated conditions.

METHODOLOGY

Pyridinyl ring-labeled [5-^{14}C]pymetrozine (MRID 44411324)

Subsamples (approximately 3.7 g) of sieved (2 mm) Les Evouettes silt loam soil (31.8% sand, 54.3% silt, 13.9% clay, 2.1% organic carbon, pH 7.3, CEC 14 mmol/Z/100 g; Table 3, p. 46) were mixed with water and placed on a glass plate to form a 2-mm thick surface (15 cm^2; p. 22) and the soil moisture was adjusted to 75% of 0.33 bar soil moisture content. Soils were treated at a nominal application rate of 11.2 ppm with pyridinyl ring-labeled [5-^{14}C]pymetrozine {6-methyl-4-(pyridine-3-yl-methylenamino)-4,5-dihydro-1,2,4-triazine-3(2H)-one; radiochemical purity 98.4%, specific activity 2.12 Mbq/mg; p. 20}, dissolved in methanol and ethyl acetate. Samples were placed in an incubation chamber maintained at 23.6 ± 0.3 °C (Appendix 5, p. 119) by circulating refrigerated water through the chamber base, and

TEXT SEARCHABLE DOCUMENT 2011

the chamber was covered with a quartz lid (p. 21). Soil temperatures were monitored using an electronic thermo logger twice daily. Humid air was passed through the chamber and drawn through ethylene glycol, 0.1 *N* H_2SO_4 and 2 *N* NaOH (50 ml each) volatile traps. Samples were irradiated on a 12-hour photoperiod using a xenon arc lamp equipped with a filter to absorb UV radiation of <290 nm (p. 20). The irradiance values (300-400 nm) at the initiation and termination of the study were determined to be 57.3 and 53.5 W/m^2, respectively (Table 2, p.45). One nominal day of incubation was equivalent to 1.5 days of exposure to natural sunlight at 40°N. Duplicate samples were removed for analysis at 0, 0.5, 1, 3, 7, 15, and 34 days posttreatment. Dark control soil samples were incubated in the same manner described for irradiated soils.

Soil samples were extracted four times with acetonitrile:water (80:20,v:v) followed by centrifugation and filtration (p. 24). Aliquots of each extract were analyzed by LSC and the supernatants were combined. Soil subsamples containing ≥10% applied radioactivity were further extracted (two sequential harsh extractions at 80-85 °C) by refluxing with acetonitrile:water (4:1; v:v) followed by centrifugation, and by refluxing with acetonitrile:0.7 N HCl (9:1; v:v) followed by centrifugation. Aliquots of each extract were analyzed by LSC. Aliquots of the extracts were concentrated to dryness and redissolved in methanol prior to analysis by two-dimensional TLC on silica gel plates developed perpendicularly with ethyl acetate:methanol:water (60:30:5;v:v:v) and chloroform:methanol:water (60:30:5;v:v:v; p. 31); the limit of quantitation was 0.058 ppm (Appendix 4, p. 118). Extracts were co-chromatographed with nonradiolabeled reference standards which were detected under UV light (254 nm); radiolabeled residues were detected and quantified by a radioimaging scanner. Following TLC analysis, the initial acetonitrile:water extracts were evaporated to dryness and redissolved in water prior to HPLC analysis (Nucleosil C-18 column) using a mobile phase gradient of water:acetonitrile (100:0 to 93:7 to 88:12 to 82:18 to 2:98; v:v) with radioactive flow detection; samples were co-chromatographed with nonradiolabeled reference standards which were visualized with UV light (298 nm; pp. 28, 29). Compound identities were further confirmed in selected samples by MS and 1H-NMR (p. 25). Nonextractable soil residues were determined by LSC following combustion (p. 24). Volatile trap solutions were replaced on each sampling date and analyzed for total radioactivity by LSC (pp. 23, 24).

To confirm the viability of the soil, a microbial analysis was performed. Subsamples of the soil were serially diluted and placed in Petri dishes with growth medium. Viability was evaluated by enumerating total colony forming units (CFU; p. 26).

Triazine ring-labeled [6-^{14}C]pymetrozine (MRID 44411325)

Subsamples (approximately 2.0 g) of sieved (2 mm) Les Evouettes silt loam soil (31.8% sand, 54.3% silt, 13.9% clay, 2.1% organic carbon, pH 7.3, CEC 14 mmol/Z/100 g; Table 3, p. 45) were mixed with water and placed on a glass plate to form a 2-mm thick surface (12 cm^2; p. 23). The soil moisture was adjusted as described previously and soils were treated at a nominal application rate of 43.8 ppm with triazine ring-labeled

TEXT SEARCHABLE DOCUMENT 2011

[6-^{14}C]pymetrozine {6-methyl-4-(pyridine-3-yl-methylenamino)-4,5-dihydro-1,2,4-triazine-3(2H)-one; radiochemical purity ≥96%, specific activity 2.02 Mbq/mg; p. 21}, dissolved in methanol and ethyl acetate. Samples were placed in an incubation chamber maintained at 23.5 ± 0.6 °C (Appendix 5, p. 126) and maintained as described previously. The irradiance values (300-400 nm) at the initiation and termination of the study were determined to be 52.7 and 48.5 W/m^2, respectively (Table 2, p.44). One nominal day of incubation was equivalent to 0.9 days of exposure to natural sunlight at 40°N. Duplicate samples were removed for analysis at 0, 0.5, 1, 3, 7, 16, and 32 days posttreatment. Dark controls were incubated as described previously.

Soil samples were extracted and the extracts were analyzed as described for the pyridinyl label study with the exception that the limit of quantitation for TLC analysis was 0.25 ppm (Appendix 4, p. 125). Nonextractable soil residues and volatiles were determined by as described previously.

DATA SUMMARY

Pyridinyl ring-labeled [5-^{14}C]pymetrozine (MRID 44411324)

Pyridinyl ring-labeled [5-^{14}C]pymetrozine (radiochemical purity 98.4%), at a nominal application rate of 11.2 ppm, degraded with a registrant-calculated half-life of 4.3 sunlight equivalent days (40° N) on Les Evouettes silt loam soil adjusted to 75% of 0.33 bar moisture content and incubated at 23.6 ± 0.3° C for 34 days while irradiated with a xenon arc lamp (12 hours of light per day; p. 40; Figure 22, pp. 74-76). In contrast, the parent compound degraded in dark controls with a registrant-calculated half-life of 10.4 days. Biphasic degradation was observed. The reviewer-calculated photolytic half-life was determined to be 6.22 days. In irradiated soils, the parent compound was initially present at 102.0% of the applied radioactivity, decreased to 53.0% of the applied by 3 days posttreatment and was present at 8.4% of the applied at 34 days (Table 7, p. 50). In contrast, the parent in dark controls was initially present at 102.0% of the applied radioactivity, decreased to 59.1% of the applied by 7 days posttreatment and was 24.5% of the applied at 34 days (Table 8, p. 51). The major degradate

4,5-dihydro-5-hydroxy-6-methyl-4-[(3-pyridinylmethylene)amino]-1,2,4-triazine-3-(2H)-one (M2)

was present in the irradiated soils at 16.3% of the applied radioactivity at 0.5 days posttreatment, was a maximum of 28.6% of the applied at 7 days, and was present at 9.1% at 34 days. In contrast, M2 in dark controls increased throughout the incubation period to a maximum of 46.6% of the applied radioactivity by 34 days posttreatment. The minor degradate 3-pyridine carboxaldehyde (M4) was present at maximums of 5.9% (day 34) and 7.6% (day 15) of the applied radioactivity in the irradiated and dark control samples, respectively. Two unidentified degradates were each detected once at ≤4.1% of the applied radioactivity in the irradiated samples.

TEXT SEARCHABLE DOCUMENT 2011

Nonextractable[^{14}C]residues were present at maximums of 50.1% of the applied radioactivity in the irradiated samples and 15.7% in the dark control samples following 34 days of incubation (Table 5, 6; pp. 48, 49). Radiolabeled $^{14}CO_2$ accounted for 25.8% and 6.0% of the applied radioactivity at 34 days posttreatment for the irradiated and dark control samples, respectively.

Material balances for the irradiated soil samples were 90.9-104.7% of the applied radioactivity throughout the incubation period.

Triazine ring-labeled [6-^{14}C]pymetrozine (MRID 44411325)

Triazine ring-labeled [6-^{14}C]pymetrozine (radiochemical purity ≥96%), at a nominal application rate of 43.8 ppm, degraded with a registrant-calculated half-life of 1.6 sunlight equivalent days (40° N) on Les Evouettes silt loam soil adjusted to 75% of 0.33 bar moisture content and incubated at 23.5 ± 0.6° C for 32 days while irradiated with a xenon arc lamp (12 hours of light per day; p. 40; Figure 19, pp. 70-72). In contrast, the parent degraded in dark controls with a registrant-calculated half-life of 5.9 days. Biphasic degradation was observed. The reviewer-calculated photolytic half-life was determined to be 4.4 days. In irradiated soils, the parent compound was initially present at 101.8% of the applied radioactivity, decreased to 61.3% of the applied by 1 day posttreatment and was 7.6% of the applied at 32 days (Table 7, p. 49). In contrast, the parent in dark controls was initially present at 97.4% of the applied radioactivity, decreased to 50.3% of the applied by 7 days posttreatment and was 24.8% of the applied at 32 days (Table 8, p. 50). The major degradate

4,5-dihydro-5-hydroxy-6-methyl-4-[(3-pyridinylmethylene)amino]-1,2,4-triazine-3-(2H)-one (M3)

was present in the irradiated samples at 16.2% of the applied radioactivity at 0.5 days posttreatment, was a maximum of 33.5% of the applied at 3 days, and was 7.4% at 32 days. In contrast, M3 in dark controls was present at a maximum of 56.1% of the applied radioactivity at 16 days posttreatment and was 47.2% of the applied at 32 days. The minor degradate 4-amino-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione (M5) was present at maximums of 5.4% (day 16) and 5.7% (day 32) of the applied radioactivity for the irradiated and dark control samples, respectively. Two unidentified degradates were each detected at ≤0.9% of the applied radioactivity.

Nonextractable [^{14}C]residues were maximums of 45.2% of the applied radioactivity in irradiated samples and 18.5% in dark control samples following 32 days of incubation (Table 5, 6; pp. 47, 48). Radiolabeled $^{14}CO_2$ accounted for 22.2% and 2.1% of the applied radioactivity at 32 days posttreatment for the irradiated and dark control samples, respectively.

Material balances for the irradiated soil samples were 89.3-107.0% of the applied radioactivity throughout the incubation period.

TEXT SEARCHABLE DOCUMENT 2011

COMMENTS

1. Les Evouettes silt loam soil was used in this study, while Hanford sandy loam soil was used in the aerobic soil metabolism study (MRID 44024965, p. 21). Subdivision N Guidelines require that the same type of soil used in the aerobic soil metabolism study be used in the photodegradation on soil study. Also, the reviewer could not confirm whether the soil used in this study was a domestic soil, or whether it was classified using the particle sizes under the USDA system.
2. The registrant used a two-component model regression line to calculate degradation rate constants (k), and calculated DT_{50}'s (actually half-lives) using the k values for rapid-phase degradation, slow-phase degradation and overall degradation (Table 9 in each study). After evaluating the data and calculating half-lives to compare with the registrant-reported values, the reviewer chose to report the overall DT_{50} as the registrant-calculated half-life. The reviewer notes that the registrant-calculated half-lives for the parent in irradiated soils were reported in terms of sunlight equivalent days at 40° N. It is also noted, however, that data for the parent compound and its degradates in irradiated soils are reported for sampling intervals described in terms of nominal days. Entries in Table 7 of each study indicate the relationship between the nominal days (sampling intervals) and sunlight equivalent days at 40° N.

3. A method development study (MRID 44411323) was provided for review. The reviewer noted that no new information was provided beyond that already reported in the two studies (pyridinyl and triazine labels).

4. The pyridinyl ring-labeled [5-^{14}C]pymetrozine dissipated with reviewer-calculated photolytic half-life of 6.2 days. The triazine ring-labeled [6-^{14}C]pymetrozine dissipated with a reviewer-calculated photolytic half-life of 4.4 days. These values were adjusted for degradation in the dark controls and indicate the half-life of the compound due solely to photodegradation.

5. The reviewer noted that in the pyridinyl label study (MRID 44411324), the degradate designated as M2 had the same structural formula as the degradate M3 in the triazine label study (MRID 44411325). Also, both studies reported separate unidentified degradates designated as M3 and M2, respectively.

6. The study author stated that degradates analyzed by 1H-NMR and MS were combined with similar degradates from a soil metabolism study to obtain sufficient samples for analysis (MRID 44411325; p. 38).

7. The methods were poorly organized in MRID 44411325 (triazine label study), and the reviewer was unclear when and under what conditions HPLC analysis was conducted.

8. The reviewer noted that the study author inadvertently stated in the title of MRID 44411325 that the 5 carbon on the triazine ring was radiolabeled; it was the 6 carbon that was labeled.

TEXT SEARCHABLE DOCUMENT 2011

9. The reviewer notes that different half-lives (in both irradiated and dark control samples) determined for the parent compound in the two studies reviewed were attributed to the different application rates utilized for the two radiolabeled parent compounds.