Lysimeter Study of Pymetrozine

Reports: Lightle, S.; Coody, P. (1997) Soil Dissipation of (carbon 14)CGA-215944 Under Actual Field Conditions in California: Interim Report: Lab Project Number: 1053: 280-96: 1973. Unpublished study prepared by PTRL East, Inc. and ABC Labs., California. 285 p.

Lightle, S.; Coody, P.; Atkins, R. (2000) Soil Dissipation of (carbon 14)CGA-215944 Under Actual Field Conditions in California: Final Report: Lab Project Number: 1053: 280-96. Unpublished study prepared by PTRL East, Inc., PTRL West, Inc. and Agvise Laboratories, Inc. 561 p.

Marsh, J.; Atkins, R. (2000) Frozen Storage Stability of (carbon 14)CGA-215944 in Soil from California: Final Report: Lab Project Number: 1061: 394-96. Unpublished study prepared by PTRL East, Inc. 121 p.

Document No.: MRIDs 44411341, 45208705, 45208707

Guideline: Not a guideline study

Classification: This study is not a guideline study, but is classified as Supplemental. This study is scientifically valid and provides supplemental information on the terrestrial field dissipation of pymetrozine in lysimeter bareground plots of loamy sand soil in California. However, a major leachate component was not characterized and pymetrozine was not shown to be stable in freezer storage for the entire duration of the study.

This original Data Evaluation Review (DER) (attached) did not include a review of MRIDs 45208705 and 45208707; therefore, a review is included below as an addendum to the original DER.

PC Code: 101103

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Background

This study was not submitted as a guideline study, but as a supplement to the terrestrial field dissipation studies. The original study (MRID 44411341) provides initial field dissipation data for pymetrozine (CGA-215944) in lysimeter bareground plots of loamy sand soil in California. Addendum 1 (MRID 45208705) was submitted after the original review, and contains the completed data through the entire length of the study. MRID 45208707 contains frozen storage stability results for pymetrozine. The following review is for MRIDs 45208705 and 45208707.

MRID 45208705

Summary

Refer to the original DER (attached) or MRID 44411341 for the introduction, materials, and methods.

The major soil degradates in the study were CO_2 (detected in a "mini-lysimeter" closed system study), CGA-359009, CGA-294849, GS-21399, CGA-215525, and CGA-300407. Bromide was used as a tracer and had breakthrough into leachate approximately 70 days after treatment. Pymetrozine was generally detected in leachate samples between 39-53 days after treatment. Pymetrozine mobility with the triazine moiety reached 24-30 inches, and 12-18 inches for the pyridine label. The major leachate components were parent, CGA-294849, and an unknown compound. The unknown compound was the most prominent leachate analyte. Due to the original natural rainfall conditions, lysimeters received 335% of the typical cumulative rainfall, rather than the 120% in the original protocol.

MRID 45208706

Summary

The frozen storage stability study was conducted to quantify the stability of pymetrozine in frozen soil used in environmental field studies. Tujunga loamy sand soil treated with either the pyridine or triazine radiolabel was stored in the freezer for up to 555 days.

Total radiocarbon recovery on average for the triazine label samples was 100.9%. Analytical results from soil treated with the triazine moiety indicated that the total percent applied radioactivity (extract 1 and 2 totaled) was found that parent ranged from 86.8-95.4% throughout the 555 days of frozen storage. CGA-215525 was detected and ranged from 0 – 10.4% throughout the study. An unknown compound ranged in percent applied radioactivity of 0.5-2.1%.

Total radiocarbon recovery on average for pyridine label samples was 97.1%. Analytical results from soil treated with the pyridine moiety indicated that the total percent applied radioactivity (extract 1 and 2 totaled) was found that parent ranged from 84.4-92.5% throughout the 555-day study. CGA-300407 was detected and ranged from 0.3-7.8% throughout the study. The percent of applied radiocarbon present as unknown was 0.9% in one pyridine sample.

The study author claims that no pattern of degradation in frozen soil was observed, however >10% of a degradate (CGA-215525) was formed by the end of the study, signaling that pymetrozine is not completely stable in frozen conditions for 555 days, but the data show that pymetrozine is stable up to 450 days in frozen storage.

Table I. Physicochemical Characteristics of the Soil Collected from Three Lysimeters and Six Depths within the Study Area.

Soil Depth	Lysimeter	Sand % (w/w)	Silt % (w/w)	Clay % (w/w)	USDA Texture Classification	Bulk Density (g/cc)	Cation Exchange Capacity (meq M+/100g)	Water Holding Capacity at: 1/3 Bar % (w/w)	Water Holding Capacity at: 15 Bar % (w/w)	Organic Matter % (w/w)	Organic Carbon [a] % (w/w)	pH (Std. Units)
0-3"	30	70	22	8	Sandy Loam	1.43	5.9	10.7	3.3	0.5	0.3	6.6
	15	68	24	8	Sandy Loam	1.44	5.6	9.8	3.4	0.4	0.2	7.3
	1	70	24	6	Sandy Loam	1.39	4.4	9.8	3.2	0.4	0.2	7.4
	Average	**69**	**23**	**7**	**Sandy Loam**	**1.42**	**5.3**	**10.1**	**3.3**	**0.4**	**0.2**	**7.1**
3-6"	30	68	24	8	Sandy Loam	1.43	6.1	11.7	3.6	0.4	0.2	6.5
	15	70	22	8	Sandy Loam	1.46	5.9	10.0	3.5	0.4	0.2	7.2
	1	72	22	6	Sandy Loam	1.39	5.7	9.7	3.3	0.3	0.2	7.3
	Average	**70**	**23**	**7**	**Sandy Loam**	**1.43**	**5.9**	**10.5**	**3.5**	**0.4**	**0.2**	**7.0**
6-12"	30	66	24	10	Sandy Loam	1.47	6.0	10.7	3.7	0.3	0.2	6.7
	15	70	22	8	Sandy Loam	1.43	5.2	9.1	3.1	0.3	0.2	7.3
	1	82	12	6	Loamy Sand	1.43	4.1	7.7	2.8	0.2	0.1	7.4
	Average	**73**	**19**	**8**	**Sandy Loam**	**1.44**	**5.1**	**9.2**	**3.2**	**0.3**	**0.1**	**7.1**
12-18"	30	66	24	10	Sandy Loam	1.46	5.8	11.7	3.7	0.3	0.2	6.9
	15	80	16	4	Loamy Sand	1.48	4.8	7.3	2.7	0.2	0.1	6.7
	1	82	12	6	Loamy Sand	1.41	4.4	7.1	2.5	0.1	0.1	7.8
	Average	**76**	**17**	**7**	**Sandy Loam**	**1.45**	**5.0**	**8.7**	**3.0**	**0.2**	**0.1**	**7.1**
18-24"	30	68	24	8	Sandy Loam	1.48	5.6	11.1	3.5	0.4	0.2	7.0
	15	84	12	4	Loamy Sand	1.49	3.8	5.8	2.2	0.1	0.1	7.2
	1	84	12	4	Loamy Sand	1.41	3.7	7.0	2.4	0.1	0.1	7.8
	Average	**79**	**16**	**5**	**Loamy Sand**	**1.46**	**4.4**	**8.0**	**2.7**	**0.2**	**0.1**	**7.3**
24-30"	30	66	24	10	Sandy Loam	1.47	6.0	11.3	3.9	0.3	0.2	6.5
	15	88	10	2	Sand	1.47	3.1	5.2	2.1	0.2	0.1	7.0
	Average	**77**	**17**	**6**	**Loamy Sand**	**1.47**	**4.6**	**8.3**	**3.0**	**0.3**	**0.1**	**6.8**
30-32"	30	62	28	10	Sandy Loam	1.44	6.7	9.4	4.1	0.3	0.2	5.6

[a] Organic carbon (%) determined per PTRL East, Inc. SOP, % organic carbon = % organic matter / 1.9.

limited mobility of radiocarbon >LOA reaching to the 24-30" soil layer over time. Downward movement of the radiolabel associated with the pyridine moiety was primarily in the first 6" with levels above the LOA of 5 ppb found at greater depths (maximum depth 12-18") only after 180 DAT in the range of 7-14 ppb.

The following radiolabeled products were identified in the upper 6 inches of soil (Tables XVII-XX):

Compound	Sampling Date (DAT)	Maximum % of Dose	Concentration (µg/g)
CGA-215944	0	88.8	1.386
CGA-359009	29	6.5	0.094
CGA-294849	29	2.6	0.038
GS-23199	4 and 29	0.2	0.003
CGA-215525	61	1.1	0.014
CGA-300407	61	5.5	0.080

Leachate collected as single leachate fractions below the lysimeters accounted for a maximum of 0.21% of dose for the triazine labelled lysimeters and 0.04% of dose for the pyridine labelled lysimeters. No leachate samples above LOA were collected for the pyridine label. The following radiolabelled products were identified in the leachate:

Compound	Lysimeter	Sample Collection DAT	Maximum % of Dose	Concentration µg/l
CGA-215944	22	53	<0.01	8.43
CGA-294849	40	124	0.03	4.45
GS-23199	32	365	0.01	3.68
CGA-359009	22	47	0.01	9.60
Unknown 3	13	103	<0.01	1.01
Unknown 2	22	47	<0.01	1.97
Unknown 1	13	120	0.19	17.60

When lysimeters showing physical anomalies resulting in ^{14}C residues showing up prior to KBr breakthrough are eliminated from the sample set, only two major constituents are found consistently in leachate, CGA-294849 and Unknown 1. Their maximum residue concentrations are the same as those presented above (Table XXII).

Table X. Summary of Characterization of Soil Samples Treated with Triazine[^{14}C]CGA-215944.

Days of Frozen Storage	Sample	Soil Extract	% of Applied as CGA-215944	% of Applied as CGA-215525	Total % of Applied Dose
0	1061-34	1	94.6	ND [a]	94.6
		2	ND	ND	ND
		Total	**94.6**	**0.0**	**94.6**
	1061-40	1	96.1	ND	96.1
		2	ND	ND	ND
		Total	**96.1**	**0.0**	**96.1**
		Average	**95.4**	**0.0**	**95.4**
18	1061-35	1	91.9	2.1	94.0
		2	ND	ND	ND
		Total	**91.9**	**2.1**	**94.0**
	1061-48	1	88.7	3.5	92.2
		2	ND	ND	ND
		Total	**88.7**	**3.5**	**92.2**
		Average	**90.3**	**2.8**	**93.1**
32	1061-47	1	85.3	3.8	89.1
		2	3.2	0.3	3.5
		Total	**88.5**	**4.1**	**92.6**
	1061-49	1	88.0	5.8	93.8
		2	ND	ND	ND
		Total	**88.0**	**5.8**	**93.8**
		Average	**88.3**	**5.0**	**93.2**
60	1061-32	1	87.8	4.8	92.6
		2	ND	ND	ND
		Total	**87.8**	**4.8**	**92.6**
	1061-41	1	88.9	3.7	92.6
		2	ND	ND	ND
		Total	**88.9**	**3.7**	**92.6**
		Average	**88.4**	**4.3**	**92.6**
120	1061-38	1	87.7	1.8	89.5
		2	ND	ND	ND
		Total	**87.7**	**1.8**	**89.5**
	1061-55	1	90.7	ND	90.7
		2	ND	ND	ND
		Total	**90.7**	**0.0**	**90.7**
		Average	**89.2**	**0.9**	**90.1**

[a] None detected.

Table X (Continued). Summary of Characterization of Soil Samples Treated with Triazine[^{14}C]CGA-215944.

Days of Frozen Storage	Sample	Soil Extract	% of Applied as CGA-215944	% of Applied as CGA-215525	Total % of Applied Dose
179	1061-46	1	89.2	2.0	91.2
		2	ND	ND	ND
		Total	**89.2**	**2.0**	**91.2**
	1061-53	1	83.9	3.5	87.4
		2	5.8	ND	5.8
		Total	**89.7**	**3.5**	**93.2**
		Average	**89.5**	**2.8**	**92.2**
270	1061-52	1	91.8	1.1	92.9
		2	ND	ND	ND
		Total	**91.8**	**1.1**	**92.9**
	1061-58	1	86.6	1.8	88.4
		2	ND	ND	ND
		Total	**86.6**	**1.8**	**88.4**
		Average	**89.2**	**1.5**	**90.7**
365	1061-39	1	90.9	1.0	91.9
		2	ND	ND	ND
		Total	**90.9**	**1.0**	**91.9**
	1061-54	1	89.6	3.3	92.9
		2	ND	ND	ND
		Total	**89.6**	**3.3**	**92.9**
		Average	**90.3**	**2.2**	**92.4**
450	1061-51	1	86.1	2.9	89.0
		2	5.1	0.4	5.5
		Total	**91.2**	**3.3**	**94.5**
	1061-57	1	84.5	4.2	88.7
		2	5.6	0.3	5.9
		Total	**90.1**	**4.5**	**94.6**
		Average	**90.7**	**3.9**	**94.6**
555	1061-33	1	83.6	10.3	93.9
		2	6.1	ND	6.1
		Total	**89.7**	**10.3**	**100.0**
	1061-56	1	78.8	9.9	88.7
		2	5.0	0.5	5.5
		Total	**83.8**	**10.4**	**94.2**
		Average	**86.8**	**10.4**	**97.1**

[a] None detected.

Table XI. Summary of Characterization of Soil Samples Treated with Pyridine[^{14}C]CGA-215944.

Days of Frozen Storage	Sample	Soil Extract	% of Applied as CGA-215944	% of Applied as CGA-300407	Total % of Applied Dose
0	1061-3	1	87.3	ND [a]	87.3
		2	4.0	0.6	4.6
		Total	**91.3**	**0.6**	**91.9**
	1061-21	1	90.7	ND	90.7
		2	ND	ND	ND
		Total	**90.7**	**0.0**	**90.7**
		Average	**91.0**	**0.3**	**91.3**
18	1061-11	1	88.7	ND	88.7
		2	4.2	ND	4.2
		Total	**92.9**	**0.0**	**92.9**
	1061-25	1	91.5	1.6	93.1
		2	ND	ND	ND
		Total	**91.5**	**1.6**	**93.1**
		Average	**92.2**	**0.8**	**93.0**
32	1061-19	1	84.3	3.5	87.8
		2	2.9	0.4	3.3
		Total	**87.2**	**3.9**	**91.1**
	1061-28	1	86.9	3.8	90.7
		2	ND	ND	ND
		Total	**86.9**	**3.8**	**90.7**
		Average	**87.1**	**3.9**	**90.9**
60	1061-18	1	87.5	1.9	89.4
		2	4.2	ND	4.2
		Total	**91.7**	**1.9**	**93.6**
	1061-24	1	82.3	3.1	85.4
		2	3.8	ND	3.8
		Total	**86.1**	**3.1**	**89.2**
		Average	**88.9**	**2.5**	**91.4**
120	1061-22	1	89.5	ND	89.5
		2	ND	ND	ND
		Total	**89.5**	**0.0**	**89.5**
	1061-30	1	86.9	1.7	88.6
		2	4.1	0.4	4.5
		Total	**91.0**	**2.1**	**93.1**
		Average	**90.3**	**1.1**	**91.3**

[a] None detected.

Table XI (Continued). Summary of Characterization of Soil Samples Treated with Pyridine[^{14}C]CGA-215944.

Days of Frozen Storage	Sample	Soil Extract	% of Applied as CGA-215944	% of Applied as CGA-300407	Total % of Applied Dose
179	1061-9	1	85.7	0.6	86.3
		2	5.1	0.5	5.6
		Total	**90.8**	**1.1**	**91.9**
	1061-27	1	86.7	1.3	88.0
		2	6.0	ND [a]	6.0
		Total	**92.7**	**1.3**	**94.0**
		Average	**91.8**	**1.2**	**93.0**
270	1061-17	1	87.9	2.4	90.3
		2	ND	ND	ND
		Total	**87.9**	**2.4**	**90.3**
	1061-26	1	88.2	2.2	90.4
		2	ND	ND	ND
		Total	**88.2**	**2.2**	**90.4**
		Average	**88.1**	**2.3**	**90.4**
365	1061-2	1	88.6	1.6	90.2
		2	ND	ND	ND
		Total	**88.6**	**1.6**	**90.2**
	1061-20	1	85.5	2.6	88.1
		2	4.1	ND	4.1
		Total	**89.6**	**2.6**	**92.2**
		Average	**89.1**	**2.1**	**91.2**
450	1061-7	1	92.6	0.8	93.4
		2	ND	ND	ND
		Total	**92.6**	**0.8**	**93.4**
	1061-8	1	87.5	0.5	88.0
		2	4.8	0.7	5.5
		Total	**92.3**	**1.2**	**93.5**
		Average	**92.5**	**1.0**	**93.5**
555	1061-6	1	80.2	5.8	86.0
		2	4.8	1.3	6.1
		Total	**85.0**	**7.1**	**92.1**
	1061-14	1	78.8	6.3	85.1
		2	4.9	2.2	7.1
		Total	**83.7**	**8.5**	**92.2**
		Average	**84.4**	**7.8**	**92.2**

[a] None detected.

50 (+/- 0.5) g Soil Sample

↓

Extract 1

Add 50 ml of acetonitrile:0.5N NH_4OH (4:1, v/v) and shake for approximately 30 minutes, centrifuge and decant. Extract three times, combining the supernatants and radioassaying.

Concentrate to approximately 15-20 mL by rotary evaporation, filter and radioassay. HPLC analyze.

↓

Extract 2

Add 50 ml of acetone:1.0N acetic acid (3:1, v/v) to previously extracted soil. Shake approximately 30 minutes, centrifuge and decant. Extract twice, combining the supernatants and radioassaying.

Concentrate to approximately 15 mL by rotary evaporation, and radioassay. HPLC analyze.

↓

Extract 3

Add 100 ml of acetonitrile:1.0N NH_4OH (4:1, v/v) to previously extracted soil. Reflux 2 hours, centrifuge, decant and radioassay.

↓

Oxidation

Air dry residual soil, grind in a mortar with pestle, oxidize subsamples.

Figure 2. Extraction Methodology Used to Analyze Soil.

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DATA EVALUATION RECORD

STUDY 10

CHEM 101103 Pymetrozine §164-1
CAS No. 123312-89-0
FORMULATION--06--WETTABLE POWDER

STUDY ID 44411341
Lightle, S. and P. N. Coody. 1997. Soil dissipation of [^{14}C]CGA-215944 under actual field conditions in California. Interim report. PTRL Project ID: 1053. Novartis Study No.: 280-96. Unpublished study performed by PTRL East, Inc., Richmond, KY (analytical phase); and ABC Laboratories, Madera, CA (in-life phase); and submitted by Novartis Crop Protection, Inc., Greensboro, NC.

DIRECT REVIEW TIME = 70 Hours

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CONCLUSIONS

Field Dissipation - Terrestrial

1. This study is scientifically valid and provides supplemental information on the terrestrial field dissipation of pymetrozine (CGA-215944) in lysimeter-enclosed bareground plots of loamy sand soil in California.

2. This study was not submitted as a guideline study, but as a supplemental study in addition to studies conducted according to Subdivision N, Series 164-1 Guidelines. Additionally, the reviewed study was an interim report and did not contain complete data sets; the anticipated length of the full study was 18 months.

3. Uniformly triazine ring-labeled [^{14}C]pymetrozine (50 WP) and uniformly pyridine ring-labeled [^{14}C]pymetrozine, applied at a nominal rate of 748 g a.i./A to lysimeter-enclosed bareground plots of Tujunga loamy sand soil in California, dissipated with registrant-calculated half-lives of 15.0 days (0 to 14 day data; $r^2 = 0.90$) and 20.4 days (0 to 14 day data; $r^2 = 0.91$), respectively; half-lives were determined from parent compound detected in the 0- to 3-inch depth only, which may have affected half-life estimations. The half-life determined for the pyridine label study may have been underestimated, as the apparent half-life was greater than 61 days posttreatment. The degradation of the compound (both labels) was biphasic with degradation occurring more slowly in the second phase, for which registrant-calculated half-lives of 1269 days (14 to 96 day data; $r^2 = 0.051$) for the triazine label and 297 days (14 to 180 day data; $r^2 = 1.0$) for the pyridine label were determined.

   Uniformly triazine ring-labeled [^{14}C]pymetrozine was initially present in the 0- to 3-inch depth at 1.3 ppm, decreased to 0.90 ppm by 7 days posttreatment, and was 0.62-0.77 ppm at 14-96 days. Residues detected below the 3-inch depth were not characterized. Degradate data are reported in parent equivalents. In the 0- to 3-inch depth, the major degradate CGA-359009 was a maximum of 0.094 ppm (29 days) and was 0.028 ppm at 96 days posttreatment. The major degradate CGA-294849 was a maximum of 0.038 ppm (29 days) and was last detected at 0.008 ppm (one replicate) at 61 days posttreatment. The minor degradate GS-23199 was detected sporadically and was a maximum of 0.005 ppm (one replicate) at 29 days posttreatment. The minor degradate CGA-215525 was detected sporadically and was a maximum of 0.010 ppm (one replicate) at 1 day posttreatment. Total [^{14}C]residues (in parent equivalents) were present in the 3- to 6-inch, 6- to 12-inch, 12- to 18-inch, and 18- to 24-inch depths at maximums of 0.083 ppm (96 days), 0.027 ppm (96 days), 0.016 ppm (180 days), and 0.009 ppm (14 days; one replicate), respectively.

   Uniformly pyridine ring-labeled [^{14}C]pymetrozine (CGA-215944) was initially present in the 0- to 3-inch depth at 1.2 ppm, decreased to 0.66 ppm by 61 days posttreatment, and was 0.49 ppm (one replicate) at 180 days posttreatment. Residues detected below the 3-inch

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depth were not characterized. Degradate data are reported in parent equivalents. In the 0- to 3-inch depth, the major degradate CGA-359009 was present at a maximum of 0.054 ppm at 4 days posttreatment and was last detected at 0.049 ppm at 14 days posttreatment. The major degradate CGA-300407 was a maximum of 0.080 ppm at 61 days posttreatment and was 0.027 ppm at 180 days posttreatment. An unidentified major degradate was detected once at 0.034 ppm (one replicate) at 180 days posttreatment. Total [^{14}C]residues (in parent equivalents) were present in the 3- to 6-inch, 6- to 12-inch, and 12- to 18-inch depths at maximums of 0.074 ppm (180 days posttreatment), 0.014 ppm (180 days posttreatment), and 0.011 ppm (14 days posttreatment; one replicate), respectively.

METHODOLOGY

Uniformly triazine ring-labeled [^{14}C]pymetrozine (50 WP; radiochemical purity 98.7%, specific activity 12.1 µCi/mg; Figure 1, p. 72) and uniformly pyridine ring-labeled [^{14}C]pymetrozine (radiochemical purity 97.5%; specific activity 12.4 µCi/mg) were applied once at a nominal rate of 748 g a.i./A (5.99 mg/lysimeter) to 8-inch diameter steel lysimeter-enclosed bareground plots (1% slope; p. 18) of Tujunga loamy sand soil (characterization data not reported) in Madera, CA. The plot contained 56 cylindrical, steel lysimeters (38-inch length; 8-inch i.d.) inserted vertically into the soil to a target depth of 36 inches (leaving the rim two inches above the soil surface). The lysimeters were inserted along an access trench (4 feet x 71 feet x 5.5 feet), and a glass leachate collection apparatus was placed under the soil columns (p. 19). The lysimeters remained untreated for approximately 26 days prior to the initiation of the study and were irrigated at 7-day intervals during that time. An overflow collection apparatus, consisting of a tube inserted through the rim (one inch above the soil surface) connected to an aluminum-foil covered glass jar, was used to collect water that pooled on the top of the soil surface as a result of heavy rainfall. The soil surfaces within 49 lysimeters were individually treated drop-wise around the inner six-inch area with triazine or pyridine ring-labeled test solution using a glass Pasteur pipette (p. 21). Of the remaining lysimeters, three were utilized as untreated controls (p. 20) and four were treated with 972 mg (178 lb Br $^{-}$/A) KBr, dissolved in water, to monitor the wetting front associated with the pesticide treatment (p. 21). Maintenance pesticides were not applied during the in-life phase of the study. The plot history for the preceding five years was not reported. Environmental data were collected on-site (Appendices 3-5, pp. 114-124, 126, 128). The depth to the water table was not reported. Precipitation was supplemented by irrigation; total water input via precipitation and irrigation was 449% (reviewer-calculated) of the 30-year historical precipitation average (Appendix 5, p. 128). Pan evaporation data were not reported.

Soil lysimeters were collected at 0, 1, 4, 7, 14, 29, 61, 96, and 180 days posttreatment for the triazine label study and at 0, 4, 14, 61, and 180 days posttreatment for the pyridine label study (Table I, p. 55). Control soil lysimeters were collected at 1 and 61 days posttreatment. Samples were collected by removing the entire lysimeter from the plot (p. 22). For the 0 day samples, the 0- to 3-inch depth was removed from the lysimeter in the field and frozen prior to shipping. All other lysimeters were sealed (top and bottom) intact

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and shipped frozen to the analytical laboratory. The soil columns within the lysimters were divided into 3-inch (to 6-inches) or 6-inch (6- to 36-inches) sections and homogenized (pp. 23, 26). The soil samples were placed into plastic bags and stored frozen until analysis. Prior to extraction, three subsamples of soil from each sampling interval and depth were collected and analyzed for total radioactivity by LSC following combustion; the limits of detection and quantitation were 2 ppb (pp. 14, 27). Soil samples were homogenized again if the coefficient of variation between the three soil subsamples was greater than 15% following LSC analysis. Control soil cores were collected and used to quantify background radioactivity and to determine the gravimetric water content in each layer of the test soil (p. 24).

Soil samples (100 g) were extracted three times by shaking with acetonitrile:0.5 N ammonium hydroxide (4:1, v:v) and centrifuged (p. 29; Figure 4, p. 78). The supernatants were decanted and combined, and triplicate aliquots were analyzed for total radioactivity by LSC. The extracts were concentrated, filtered, and analyzed by reverse-phase HPLC (Alltima C18 column; p. 18) using a mobile phase gradient of 1% acetonitrile and 0.1% trifluoroacetic acid in water (pH 2):0.05% trifluoroacetic acid in methanol (100:0 to 93:7 to 88:12 to 82:18 to 50:50 to 0:100, v:v) with radioactive flow detection (pp. 30-31); eluate fractions were collected and analyzed for total radioactivity by LSC. Samples were co-chromatographed with nonradiolabeled reference standards which were located by UV light (220 nm). Soil samples for which recoveries were less than 90% of the total radioactivity remaining in the soil following the previous extraction were further extracted by shaking with acetone:1 N acetic acid (3:1, v:v) and centrifuged. Supernatants were decanted and combined, and aliquots were analyzed by LSC and HPLC as previously described. Soil samples for which recoveries were less than 90% of the total radioactivity remaining in the soil following the previous extraction were further extracted by refluxing with acetonitrile:1 N ammonium hydroxide (4:1, v:v) and centrifuged. Triplicate aliquots of the extracts were analyzed for total radioactivity by LSC. Subsamples of post-extracted soil were air dried, ground to powder, and analyzed for total radioactivity by LSC following combustion.
To confirm compound identities, selected soil extracts (from the first and second extraction procedures) were analyzed using two-dimensional TLC on cellulose plates developed perpendicularly with chloroform:methanol:14.8 N ammonium hydroxide:water (80:30:2:4, v:v:v:v) followed by ethyl acetate:methanol:water (75:15:10, v:v:v); radiolabeled compounds were detected with a radioactive imaging scanner (pp. 32, 33). Sample extracts were co-chromatographed with nonradiolabeled reference standards which were located with UV light (wavelength unspecified). Areas of radioactivity were scraped from the plates, dissolved in methanol, and analyzed for total radioactivity by LSC.

Leachate accumulations were monitored at 3-day intervals and collected when leachate was present (p. 24). The jars were sealed and shipped frozen to the analytical laboratory for analysis. Triplicate aliquots were analyzed for total radioactivity by LSC (p. 27); the limit of detection was 0.5 ppb (p. 14). Overflow collection jars were also monitored at 3-day intervals and after heavy precipitation, and collected when overflow water was

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present (p. 24). The jars were sealed and shipped frozen to the analytical laboratory. Triplicate aliquots were analyzed for total radioactivity by LSC (pp. 27-28). Leachate and overflow water samples were concentrated and analyzed by HPLC as previously described for the soil samples (p. 30). Water present on top of the soil surface at the time of sampling was collected, shipped frozen to the analytical laboratory and analyzed for total radioactivity by LSC (p. 25).

DATA SUMMARY

Uniformly triazine ring-labeled [^{14}C]pymetrozine (50 WP; radiochemical purity 98.7%) and uniformly pyridine ring-labeled [^{14}C]pymetrozine (radiochemical purity 97.5%), applied at a nominal rate of 748 g a.i./A to lysimeter-enclosed bareground plots of Tujunga loamy sand soil in California, dissipated with registrant-calculated half-lives of 15.0 days (0 to 14 day data; $r^2 = 0.90$) and 20.4 days (0 to 14 day data; $r^2 = 0.91$), respectively (Figure 11, pp. 85, 86); half-lives were determined from parent compound detected in the 0- to 3-inch depth only (see Comment #5). The half-life determined for the pyridine label study may have been underestimated, as the apparent half-life was greater than 61 days posttreatment. The degradation of the compound (both labels) was biphasic with degradation occurring more slowly in the second phase, for which registrant-calculated half-lives of 1269 days (14 to 96 day data; $r^2 = 0.051$) for the triazine label and 297 days (14 to 180 day data; $r^2 = 1.0$) for the pyridine label were determined.

Uniformly triazine ring-labeled [^{14}C]pymetrozine

The parent compound was initially present in the 0- to 3-inch depth at 1.3 ppm, decreased to 0.90 ppm by 7 days posttreatment, and was 0.62-0.77 ppm from 14 to 96 days posttreatment (Table XI, pp. 65-67). Residue data were not reported for the 180-day soil samples. Residues detected below the 3-inch depth were not characterized. Degradate data are reported in parent equivalents. In the 0- to 3-inch depth, the major degradate

CGA-359009 (chemical name not reported; chemical structure presented in Figure 1, p. 74)

was initially present at 0.051 ppm at 1 day posttreatment, increased with variability to a maximum of 0.094 ppm by 29 days posttreatment, and was 0.028 ppm at 96 days posttreatment. The major degradate

1,2,4-triazine-3,5 (2H, 4H)-dione-4-amino-6-methyl (CGA-294849)

was initially present at 0.009 ppm at 1 day posttreatment, increased with variability to a maximum of 0.038 ppm by 29 days posttreatment, and was last detected at 0.008 ppm (one replicate) at 61 days posttreatment. The minor degradate GS-23199 (chemical name not reported; chemical structure presented in Figure 1, p. 72) was sporadically detected, at 0.003-0.005 ppm at 4, 14 (one replicate), and 29 (one replicate) days posttreatment. The

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minor degradate 1,2,4-triazin-3(2H)-one 4,5-dihydro-6-methyl (CGA-215525) was sporadically detected at ≤0.010 ppm from 1 to 96 days posttreatment. Two unidentified minor degradates were each detected at ≤0.007 ppm. Total [^{14}C]residues (in parent equivalents) were present in the 3- to 6-inch, 6- to 12-inch, 12- to 18-inch, and 18- to 24-inch depths at maximums of 0.083 ppm (96 days), 0.027 ppm (96 days), 0.016 ppm (180 days), and 0.009 ppm (14 days; one replicate), respectively (Table V, p. 59).

Total [^{14}C]residues detected in the leachate were 0.04-0.53% of the applied from 61 to 180 days posttreatment (Table VII, p. 61). Characterization data for the leachate were reported only for samples collected at 92, 95, 99, 103 and 106 days posttreatment. The major degradate CGA-329520 (chemical name not reported; chemical structure presented in Figure 1, p. 74) was detected at 2.8-21.1 ppb from 92 to 106 days posttreatment (Appendix 22, p. 249). The minor degradates CGA-294849 and GS-23199 were detected at 0.53-2.5 ppb (92, 95, 103 and 106 days) and 0.30 ppb (103 days), respectively.

Total [^{14}C]residues detected in the overflow water samples were 0.06-0.94% of the applied from 61 to 180 days posttreatment (Table VII, p. 61). Characterization data for the overflow water samples were only reported for two samples collected at 61 days posttreatment. The parent compound and the minor degradates CGA-294849 and CGA-359009 were detected at 1.9-4.8 ppb, 1.2-1.3 ppb and 3.1-3.3 ppb, respectively (Appendix 23, p. 251).

Uniformly pyridine ring-labeled [^{14}C]pymetrozine

The parent compound was initially present in the 0- to 3-inch depth at 1.2 ppm, decreased to 0.66 ppm by 61 days posttreatment, and was 0.49 ppm (one replicate reported) at 180 days posttreatment (Table XII, pp. 68, 69). Residues detected below the 3-inch depth were not characterized. Degradate data are reported in parent equivalents. In the 0- to 3-inch depth, the major degradate

CGA-359009

was initially present at 0.015 ppm (one replicate) at day 0, increased to a maximum of 0.054 ppm by 4 days posttreatment and was last detected at 0.049 ppm at 14 days posttreatment. The major degradate

CGA-300407 (chemical name not reported; chemical structure presented in Figure 1, p. 73)

was initially present at 0.037 ppm (one replicate) at day 0, increased to a maximum of 0.080 ppm by 61 days posttreatment and was 0.027 ppm (one replicate reported) at 180 days posttreatment. An unidentified major degradate was detected once at 0.034 ppm (one replicate reported) at 180 days posttreatment. Total [^{14}C]residues (in parent equivalents) were present in the 3- to 6-inch, 6- to 12-inch, and 12- to 18-inch depths at

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maximums of 0.074 ppm (180 days posttreatment), 0.014 ppm (180 days posttreatment), and 0.011 ppm (14 days posttreatment; one replicate), respectively (Table VI, p. 60).

Total [^{14}C]residues detected in the leachate were 0.05% of the applied at 180 days posttreatment (Table VIII, p. 62). Total [^{14}C]residues detected in the overflow water samples were 0.02-0.37% of the applied from 61 to 180 days posttreatment. Characterization data for the leachate and overflow samples were not reported.

COMMENTS

1. This study was not submitted as a guideline study, but as a supplemental study in addition to studies conducted according to Subdivision N, Series 164-1 Guidelines. Additionally, the reviewed study was an interim report and did not contain complete data sets; the anticipated length of the full study was 18 months. The reviewer notes, however, that the pesticide was applied at an exaggerated use rate which is generally not considered to be valid for the determination of the half-life of the parent compound under field conditions.

2. The study was not conducted under typical use conditions. The lysimeters (8-inch inner diameter; p. 18) were too small to be representative of actual use conditions. The method of application was atypical (glass pipette) and only limited areas of the plot (the inner 6 inches of the lysimeter) were treated (p. 21).

3. Complete characteristics of the Tujunga loamy sand soil were not reported. Subdivision N guidelines require that the test soil be characterized according to the USDA classification system. The reviewer noted that a soil series description was reported in Figure 3 (pp. 76, 77). The study authors stated that complete physical/chemical characteristics of the test site soil will be included in the final study (p. 39).

4. A reasonable attempt was not made to identify all degradates present at ≥0.01 ppm. In the pyridine label study, an unidentified major degradate was present in the soil at 0.034 ppm (one replicate) at 180 days posttreatment. Under Subdivision N Guidelines, the registrant must demonstrate that a reasonable attempt was made to identify all degradates present at ≥0.01 ppm.

5. The study authors reported that irrigation of the lysimeters following the application of the test substance may have been responsible for the rapid movement of the test compound into the 3- to 6-inch depth (pp. 41, 42). The reviewer notes that the reported half-lives were determined from 0- to 3-inch depth data; generally, field dissipation half-lives are calculated using data from the 0- to 6-inch depths. Use of the 0- to 3-inch data only, combined with the rapid movement of the test compound into the lower depth due to irrigation, may have caused the half-life of the parent compound to be underestimated.

6. It could not be determined whether monitoring adequately detected all major degradates

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identified in the aerobic metabolism studies. Two aerobic soil metabolism studies (MRIDs 44024965 and 44024966) were submitted; however, an adequate attempt was not made to extract and characterize degradates in those studies. Monitoring adequately detected all major degradates identified in two anaerobic aquatic metabolism studies (MRIDs 44024967 and 44024968) that were submitted.

7. A plot history was not provided. Additionally, no pretreatment samples were taken to confirm that the test site was not contaminated with the test substance or other related pesticides prior to application of the test substance. Subdivision N Guidelines require that the site have no previous use history involving the test compound or related compounds.

8. The maximum proposed label rate for pymetrozine (CGA-215944) was reported to be 680 g a.i./A for tree crops and 170 g a.i./A for row crops (MRID 44411334).

9. The study authors stated that the samples were shipped frozen to the analytical laboratory and placed in frozen storage until being processed for analysis (p. 23). The maximum duration for which the samples were stored and the storage temperature were not reported. The study authors stated that the frozen storage stability of the parent compound in the test soil was being evaluated in a separate study.

10. The reported registrant-calculated half-life (1269 days) for the parent compound (triazine label) during the second phase of the biphasic degradation was based on data from 14 to 180 days; however, residue data were only reported for up to 96 days (Figure 11, p. 85). Clarification by the registrant is appropriate.

11. Limits of quantitation were not reported for LSC analyses of water samples, and limits of detection and quantitation were not reported for HPLC and TLC analyses. Both limits of detection and quantitation should be reported to allow the reviewer to evaluate the adequacy of the method for the determination of the test compound and its degradates.

12. The reviewer noted that complete data were not reported for all sampling intervals. For the triazine label study, data for samples collected at 180 days posttreatment and parent data for one of the two lysimeters collected at day 0 were not reported (Table XI, pp. 65-67). In a footnote, the study authors stated that the samples from the other lysimeter collected at day 0 were not extracted or chemically analyzed by the time the study was written. For the pyridine label study, data were reported for only one lysimeter collected at 180 days posttreatment (Table XII, p. 69).

13. The study authors reported [^{14}C]residue data in units of concentration and as percentages of the applied radioactivity. The percentage data represented the percentage of the applied radioactivity detected in the entire soil segment and was calculated by multiplying the residue soil concentration (µg/g) by the mass of the soil segment. Because the mass of soil segments varied between samples, the patterns of formation and decline observed in the concentration data were different from those observed in the percentage data (which were considered to inaccurately represent the residue concentrations). Therefore, the reviewer

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reported only the concentration data.

14. Evaporative losses from the leachate and overflow collection jars were quantified (p. 25); however, data were not reported. The study authors stated that the available results demonstrated that evaporation from the collection jars, which were covered with perforated lids (overflow jars) or collection funnels (leachate jars), occurred during the short residence time (approximately 3 days) when aqueous samples were in the field. The reported leachate and overflow data were not adjusted for evaporation.

15. Material balances are not required for terrestrial field dissipation studies and are generally not reported. Because this study was conducted with radiolabeled test compounds applied in lysimeters, material balances were reported. Material balances for the triazine and pyridine label studies were 68.9-103.0% and 46.3-94.6% of the applied radioactivity, respectively, with decreasing material balances observed with time (Tables VII, VIII, pp. 61, 62). Due to the rapid loss of radioactivity (>50% of the applied by 23 days) in the pyridine label study, an additional study was conducted in Georgia, to determine the amount of $^{14}CO_2$ produced. "Mini-lysimeters" containing Tifton sandy loam soil were treated with uniformly pyridine ring-labeled [^{14}C]pymetrozine and maintained in a temperature-controlled chamber. Air was passed through the system and volatiles were collected in a series of traps (trapping solutions unspecified; p. 44). Evolved $^{14}CO_2$ accounted for 5-13% of the applied radioactivity by 15 days posttreatment. The study authors stated that the preliminary results indicated that the pyridinyl carbon undergoes rapid mineralization to $^{14}CO_2$ in the test soil and that rapid decline in radioactivity recovered in the field study was believed to be due to emission of $^{14}CO_2$ following treatment (pp. 44, 45).