Chemical Code: 120301 Date Out: 4-30-93

# ENVIRONMENTAL FATE AND GROUND WATER BRANCH

## Review Action

To: Kathy Davis, PM 52
Special Review and Reregistration Division (H7508W)

From: Paul J. Mastradone, Ph.D. Chief
Environmental Chemistry Review Section 1
Environmental Fate & Ground Water Branch/EFED (H7507C) 4/30/93

Thru: Henry M. Jacoby, Chief
Environmental Fate & Ground Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of...

| | | | |
|---|---|---|---|
| **DP Barcode:** | D184066, 184064, 170798, 167595, & 166723 | | |
| **Common Name:** | Thidiazuron | **Trade name:** | Dropp 50 WP |
| **Company Name:** | NOR-AM | | |
| **ID #:** | 120301 | | |
| **Purpose:** | Phase IV review of environmental fate data. | | |

| Type Product: | Action Code: | EFGWB #(s): | Review Time: |
|---|---|---|---|
| Cotton defoliant | 602 | 93-0136, 93-0134, 92-0185, 91-0878, & 91-0791 | 20.0 days |

**STATUS OF STUDIES IN THIS PACKAGE:**

| Guideline # | MRID | Status[1] |
|---|---|---|
| 161-1 | 42069203 | A |
| 161-2 | 41188201<br>41364910 | C |
| 161-3 | 41364902<br>00156241 | I |
| 162-1 | 41950101 | A |
| 162-2 | 41945201 | A |
| 163-1 | 41364909 | A |
| 164-1 | 41761105 | C |
| 165-1 | 00030793<br>41364907<br>41364908 | C<br>C<br>C |
| 165-4 | | |

**STATUS OF DATA REQUIREMENTS:**

| | Status[2] |
|---|---|
| | S |
| | N |
| | N |
| | P |
| | S |
| | P |
| | N |
| | N |
| | Waived |

[1]Study Status Codes: A=Acceptable U=Upgradeable C=Ancillary I=Invalid.
[2]Data Requirement Status Codes: S=Satisfied P=Partially satisfied N=Not satisfied R=Reserved.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

Chemical: Thidiazuron
PC Code: 120301
Case no: 4092
DP Barcode: 184066,184064,
170798, 167595, 166723
EFGWB nos: 93-0134, 93-0136
92-0185, 91-0791, 91-0185

MEMORANDUM

Subject: Thidiazuron - List D Phase 4 Review

From: Arnet W. Jones, Agronomist
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C)

Through: Henry Jacoby, Chief
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C)

Paul J. Mastradone, Ph.D., Chief, Review Section #1
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C)

To: Kathy Davis, Product Manager #52
Special Review and Reregistration Division (H7508W)

Enclosed is the Phase 4 review package for List D chemical Thidiazuron. The package includes DERs for nine studies and Table A which provides details concerning all applicable environmental fate data requirements.

1. Use Pattern

According to the LUIS report (09/02/92), Thidiazuron (N-phenyl-N'-(1,2,3-thiadiazyl) urea) is a cotton defoliant (ground or aerial application) used to remove cotton leaves prior to harvest. The only product (Dropp 50 WP) is formulated as a wettable powder and is contained in water soluble bags. It can be applied by ground or air at a maximum rate of 0.2 lb a.i./A, with two applications not to exceed a total of 0.3 lb a.i./A. There are restrictions against feeding gin trash and treated foliage to animals. Also, there are restrictions against planting rotational crops of 2 weeks (small grains, sorghum, corn, and root crops) to 2 months (legumes, alfalfa, or leafy vegetables) following application. The usage category is Terrestrial Food.

2. Status of Environmental Fate Data Requirements

The status of the environmental fate data requirements for thidiazuron for terrestrial food crop use is summarized below:

| Environmental Fate Data Requirements | | Status | MRID Number |
|---|---|---|---|
| **Degradation** | | | |
| 161-1 | Hydrolysis | Fulfilled (AWJ 04/28/93) | 42069203 |
| 161-2 | Photodegradation in water | Not Fulfilled (JAH 12/06/89; AWJ 04/28/93) | 41188201 41364910 |
| 161-3 | Photodegradation on soil | Not Fulfilled (AWJ 04/28/93) | 41364902 00156241 |
| 161-4 | Photodegradation in air | Not Submitted[1] | |
| **Metabolism** | | | |
| 162-1 | Aerobic soil | Partially Fulfilled (AWJ 04/28/93) | 41950101 |
| 162-2 | Anaerobic soil | Fulfilled (AWJ 04/28/93) | 41945201 |
| **Mobility** | | | |
| 163-1 | Leaching, Adsorption/ Desorption | Partially Fulfilled (AWJ 04/28/93) | 41364909 |
| 163-2 | Volatility-lab | Not Submitted[1] | |
| 163-3 | Volatility-field | Not Submitted[1] | |
| **Dissipation** | | | |
| 164-1 | Soil | Not Fulfilled (AWJ 04/28/93) | 41761105 |
| 164-5 | Soil, long-term | Reserved[2] | |
| **Accumulation** | | | |
| 165-1 | Confined rotational crops | Not Fulfilled (AWJ 04/28/93) | 00030793 41364907 41364908 |
| 165-4 | Fish | Waived[3] | |
| **Spray Drift** | | | |
| 201-1 | Droplet size spectrum | Not submitted[4] | |
| 202-1 | Drift field evaluation | Not submitted[4] | |

Footnotes:

[1] Based on the vapor pressure reported in EFGWB 's One-Liner Database (3 x $10^{-11}$ mm Hg), volatility does not appear to be an important route of dissipation. Therefore, this study is not required at this time.

[2] The long-term soil dissipation study (164-5) is reserved until evaluation of an acceptable soil dissipation study (164-1).

[3] See Waiver Request below.

[4] This study is required when aerial applications (rotary and fixed wing) and mist blower or other methods of ground application are proposed and it is estimated that the detrimental effect level of those nontarget organisms expected to be present would be exceeded. These data are required for all herbicides which are applied aerially.

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3. Environmental Fate Summary

There are insufficient data for a comprehensive environmental fate assessment for thidiazuron at this time. Preliminary data indicate that mineralization to $CO_2$ and adsorption to soil may be major routes of dissipation. These data, however, were derived from European soils which are not representative of the compound's typical use sites (i.e. U.S. cotton soils). Additional data from U.S. cotton soils are needed to assess fully the environmental fate of thidiazuron. The following assessment is based on all available information.

An acceptable study indicates that thidiazuron is stable to hydrolysis at pH 5, 7, and 9. Supplemental studies indicate that it photodegrades rapidly in water and on soil ($t_{\frac{1}{2}}$ = <1 hr). The principal soil photodegradation product was the isomer 1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea. In an aerobic soil metabolism study conducted in a German sandy loam which partially fulfilled the data requirement, thidiazuron metabolized with a half-life of 111 days. At the end of the 1-year study, $^{14}CO_2$ and bound residues comprised 21.2% and 44.7% of the applied radioactivity, respectively, indicating that mineralization to $CO_2$ and adsorption to soil may be routes of dissipation. Data regarding the formation and decline of degradation products containing the thiadiazol moiety are needed to understand more completely the aerobic soil metabolism of the compound. Thidiazuron was stable in an acceptable anaerobic soil metabolism ($t_{\frac{1}{2}}$ = >>90 days). It was slightly mobile to relatively immobile in acceptable batch equilibrium studies ($K_{ads}$ were 4.36, 16.2, 7.33, and 18.78 on sand, loamy sand, sandy loam, and clay loam soils, respectively); adsorption was related to soil organic matter content and cation exchange capacity. Aged leaching data are needed to assess the mobility of degradation products. In a supplemental study conducted for 9 months, thidiazuron did not dissipate from the upper 8 cm of a Florida sand and did not leach significantly (low concentrations of parent were detected at 15-30 cm; it was not detected deeper than 30 cm). In two supplemental studies, small amounts of thidiazuron accumulated in confined rotational crops.



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4. Accumulation in Fish (165-4) - Waiver Request

The registrant (NOR-AM) has requested a waiver of this data requirement based on the low octanol/water partition coefficient and because the estimated environmental concentration (<4 ppb) is low in comparison to the aquatic $LC_{50}$ value for daphnia (10 ppb).

The octanol/water partition coefficient ($K_{ow}$) reported by NOR-AM to the Product Manager (but not validated by HED/Product Chemistry), 58.3 (log $K_{ow}$ = 1.77), indicates that thidiazuron has low potential to bioaccumulate in fish. Accordingly, EFGWB agrees to waive the accumulation in fish data requirement (165-4) at this time provided that the $K_{ow}$ is valid and that Ecological Effects Branch does not need this information.

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
**THIDIAZURON**
Last Update on April 29, 1993
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

| LOGOUT | Reviewer: | Section Head: | Date: 04/29/93 |
|---|---|---|---|

Common Name:THIDIAZURON
Smiles Code:S(N=N1)C(=C1)NC(=O)N-c(ccc2)cc2
PC Code # :120301 CAS #:51707-55-2 Caswell #:

Chem. Name : N-PHENYL-N'-1,2,3-THIADIAZOL-5-YL UREA

Action Type: PLANT GROWTH REGULATOR; DEFOLIANT

Trade Names: DROPP; SN 49537
(Formul'tn): WP 50%
Physical State:

Use : FOR DEFOLIATION OF COTTON
Patterns :
(% Usage) :
:

Empirical Form: $C_9H_8N_4SO$
Molecular Wgt.: 220.25 Vapor Pressure: 3.00E-11 Torr
Melting Point : °C Boiling Point: °C
Log Kow : pKa: @ °C
Henry's : E Atm. M3/Mol (Measured)

| Solubility in ... | | | | | Comments |
|---|---|---|---|---|---|
| Water | E | 31 | ppm | @ °C | |
| Acetone | E | | ppm | @ °C | |
| Acetonitrile | E | | ppm | @ °C | |
| Benzene | E | | ppm | @ °C | |
| Chloroform | E | | ppm | @ °C | |
| Ethanol | E | | ppm | @ °C | |
| Methanol | E | | ppm | @ °C | |
| Toluene | E | | ppm | @ °C | |
| Xylene | E | | ppm | @ °C | |
| | E | | ppm | @ °C | |
| | E | | ppm | @ °C | |

Hydrolysis (161-1)
[V] pH 5.0:STABLE
[V] pH 7.0:STABLE
[V] pH 9.0:STABLE
[ ] pH :
[ ] pH :
[ ] pH :

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Last Update on April 29, 1993
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Photolysis (161-2, -3, -4)
[V] Water:0.4 HOUR
[ ] :
[ ] :
[ ] :

[V] Soil : 26 DAYS ON LmSd
[ ] Air :

Aerobic Soil Metabolism (162-1)
[V] 111 DAYS IN GERMAN SANDY LOAM; ADDL DATA NEEDED ON THIADIAZOL
[ ] MOIETY
[ ]
[ ]
[ ]
[ ]
[ ]

Anaerobic Soil Metabolism (162-2)
[V] STABLE IN GERMAN SANDY LOAM
[ ]
[ ]
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Anaerobic Aquatic Metabolism (162-3)
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Aerobic Aquatic Metabolism (162-4)
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Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
**THIDIAZURON**
Last Update on April 29, 1993
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Soil Partition Coefficient (Kd) (163-1)
[V] Kd = 4.36 (SAND, 0.83% OM; Koc = 908)
[V] Kd = 16.2 (LOAMY SAND, 3.55% OM; Koc = 786)
[V] Kd = 7.33 (SANDY LOAM, 1.62% OM; Koc = 780)
[V] Kd = 18.78 (SANDY CLAY LOAM, 6.55% OM; Koc = 494)
[ ] AGED LEACHING DATA STILL NEEDED TO FULFILL DATA REQUIREMENT.
[ ]

Soil Rf Factors (163-1)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Laboratory Volatility (163-2)
[ ]
[ ]

Field Volatility (163-3)
[ ]
[ ]

Terrestrial Field Dissipation (164-1)
[S] OF THREE SOILS, ONLY THE COMMERCE SiLm SOIL IN MISSISSIPPI
[ ] SHOWED A MOVEMENT ABOVE OR AT THE DETECTION LIMIT BELOW 6".
[ ]
[S] NO REPORTED DISSIP IN 0-8 CM IN 9 MONTH STUDY IN FL IN TIFTON
[ ] SANDY LOAM. NO DEGRADATES AND NO LEACHING DETECTED (04/28/93).
[ ]
[ ]
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[ ]

Aquatic Dissipation (164-2)
[ ]
[ ]
[ ]
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[ ]
[ ]

Forestry Dissipation (164-3)
[ ]
[ ]

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
**THIDIAZURON**
Last Update on April 29, 1993
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Long-Term Soil Dissipation (164-5)
[ ]
[ ]

Accumulation in Rotational Crops, Confined (165-1)
[S] SMALL QUANTITIES ACCUMULATED IN ROTATIONAL CROPS AT VARIOUS
[ ] PLANTING INTERVALS.

Accumulation in Rotational Crops, Field (165-2)
[S] LABEL RESTRICTIONS ON PLANTING UNTIL 2 WKS AFTER APPL.
[ ] FOR SMALL GRAINS; 2 MOS FOR LEGUMES, LEAFY VEGS.

Accumulation in Irrigated Crops (165-3)
[ ]
[ ]

Bioaccumulation in Fish (165-4)
[ ] WAIVED BASED ON LOW Kow (58.3). IN EARLIER STUDY, BCF FOR BLUEGILL
[ ] WAS 54X; FOR CATFISH FILLET, BCF WAS 1X.

Bioaccumulation in Non-Target Organisms (165-5)
[ ]
[ ]

Ground Water Monitoring, Prospective (166-1)
[ ]
[ ]
[ ]
[ ]

Ground Water Monitoring, Small Scale Retrospective (166-2)
[ ]
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Ground Water Monitoring, Large Scale Retrospective (166-3)
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[ ]
[ ]

Ground Water Monitoring, Miscellaneous Data (158.75)
[ ]
[ ]
[ ]

Environmental Fate & Effects Division
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Field Runoff (167-1)
[ ]
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[ ]
[ ]

Surface Water Monitoring (167-2)
[ ]
[ ]
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[ ]

Spray Drift, Droplet Spectrum (201-1)
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Spray Drift, Field Evaluation (202-1)
[ ]
[ ]
[ ]
[ ]

Degradation Products

1,2,3-thiadiazol-5-yl urea (=21% after a year in loamy sand)
Under light, parent compd. partially isomerizes in aqueous solutions or on soil to give product #2 which resists photo-degradation and has water solubility of 41-46 ppm.
At least 9 metabolites result from microbial action on the parent compound.

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
**THIDIAZURON**
Last Update on April 29, 1993
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

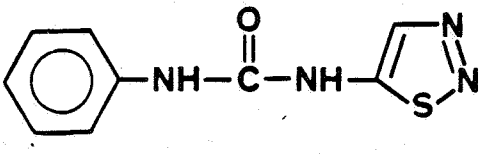
Comments

Several studies were conducted in European soils, but compound is registered only for cotton. Additional information is required for U.S. cotton soils.

References:
Writer : PJH, A W Jones

1.0 CHEMICAL:

Common Name: Thidiazuron
Chemical Name: 1-phenyl-3-(1,2,3-thidiazol-5-yl)-urea
Trade Name: Dropp
Chemical Structure:



Chemical/physical properties:

molecular weight: 220.25
solubility ($H_2O$): 31 mg/L @25°C
vapor pressure: 3 X $10^{-11}$ torr @25°C

2.0 TEST MATERIAL: See individual study reviews.

3.0 STUDY/ACTION TYPE: Review of studies in support of reregistration.

4.0 STUDY IDENTIFICATION:

The following study supplement is reviewed in this 12-pointer (see Discussion below):

Brehm, M. 1989. W63 Supplement - Thidiazuron: The photodegradation of thidiazuron in aqueous solution. Schering code no. ZK 49537; Laboratory Project ID APC 55/89. Submitted by NOR-AM Chemical Co. MRID no. 41364910; supplement to MRID no. 41188201.

The following studies are reviewed in the attached DERs:

Study 1: Tschampel, M. 1991. The determination of the rate of hydrolysis of thidiazuron. Unpublished study performed by Schering AG, Berlin, Federal Republic of Germany, and submitted by NOR-AM Chemical Co. Laboratory project ID APC 71/91. MRID no. 42069203

Study 2: Klehr, M., J. Iwan, and J. Riemann. 1983. W23 Thidiazuron: An experimental approach to the photolysis of pesticides adsorbed on soil: Thidiazuron. Pesticide Science 14:359-366. Published study performed by Schering AG, Berlin, Germany, and submitted by NOR-AM Chemical Company, Wilmington, DE. MRID no. 41364902

Study 3: Klehr, M., J. Iwan, and J. Riemann. 1981. Photodegradation of thidiazuron (SN 49537) on soil surfaces. Unpublished study performed by Schering AG, Berlin, Germany, and submitted by NOR-AM Chemical Company, Wilmington, DE. MRID no. 00156241

Study 4: Feyerabend, M. 1991. Aerobic degradation of [UL-14C]-phenyl-thidiazuron in a sandy loam soil at 21°C. Unpublished study performed by

Schering AG, Berlin, Federal Republic of Germany, and submitted by NOR-AM Chemical Co. Laboratory Project ID UPSR 21/91. MRID no. 41950101

Study 5: Feyerabend, M. 1991. Anaerobic degradation of [UL-14C]-phenyl-thidiazuron in a sandy loam soil at 21°C. Unpublished study performed by Schering AG, Berlin, Federal Republic of Germany, and submitted by NOR-AM Chemical Co. Laboratory Project ID UPSR 20/91. MRID no. 41945201

Study 6: Bruhl, R. 1988. W61 thidiazuron: Adsorption to and desorption from soil. Study No. PF-S 87 057. Report No. UPSR 17/88 - PA 49 537.7/6. Unpublished study performed by Schering AG, Berlin, Germany, and submitted by NOR-AM Chemical Company, Wilmington, DE. MRID no. 41364909

Study 7: Wrede-Rucker, A. 1990. W67 thidiazuron: Dissipation of thidiazuron in soil following application of Dropp 50WP to bare ground - USA 1989. Study No. PF-R 89 068; Report No. UPSR 65/90 - PA 49 537.7/16. Unpublished study performed by Schering AG, Berlin, Germany, and submitted by NOR-AM Chemical Company, Wilmington, DE (MRID no. 41761105)

Study 8: Bruhl, R. 1978. Rotational plant uptake study with radioactive SN 49 537. Laboratory Project ID: PA 49 537.72/6. Unpublished study performed by Schering AG and submitted by NOR AM Chem. Co. MRID no. 00030793.

Bruhl, R. 1979. Appendix to rotational plant uptake study with radioactive SN 49 537. Laboratory Project ID: PA 49 537.72/6. Unpublished study performed by Schering AG and submitted by NOR-AM Chemical Company, Wilmington, DE. Date of original study: Aug. 10, 1978. MRID no. 41364907 (appendix to Study 8).

Study 9: Bruhl, R. 1982. W48 Thidiazuron: Residues of thidiazuron in rotational crops. Laboratory Project ID: R + S 24/82-PA 49 537.75/6. Unpublished study performed by Schering AG, Berlin, Germany, and submitted by NOR-AM Chemical Company, Wilmington, DE (MRID no. 41364908)

5.0 REVIEWED BY:

Arnet W. Jones, Agronomist
Review Section 1
OPP/EFED/EFGWB

Signature: _____

Date: 8 APR 1993

6.0 APPROVED BY:

Paul J. Mastradone, Ph.D.
Chief, Review Section 1
OPP/EFED/EFGWB

Signature: _____

Date: 28 APR 1993

7.0 CONCLUSIONS:

The following environmental fate studies were submitted in support of reregistration and have been reviewed by EFGWB:

7.1 Hydrolysis

EFGWB concludes that thidiazuron is stable to hydrolysis in aqueous buffer solutions at pH 5, 7, and 9. The data requirement (161-1) is fulfilled; no additional data on the hydrolysis of thidiazuron are needed at this time.

In a 36-day study, no hydrolysis of thidiazuron (nominal concentration of 10 ppm) was reported in aqueous buffer solutions (pH 5, 7, and 9) held in darkness at 25 ± 1°C.

7.2 Photodegradation in Water (161-2)

The photodegradation in water study submitted was reviewed previously (EFGWB no. 90737; MRID no. 41188201; 12/06/89). EFGWB concluded that the study could not be used to fulfill the data requirement because: (1) the mercury arc lamp used did not have a continuous spectral distribution and the light intensity was more than three times that of natural sunlight; (2) different light sources were used in the photolysis rate and photodegradate identification studies; and (3) photodegradates were not characterized. A supplement (MRID no. 41364910) was submitted which addressed only the characterization of photodegradates.

The photolysis in water (161-2) data requirement remains unfulfilled because the supplement submitted did not correct two of the major problems which led to rejection of the original study. A new photodegradation in water study is needed. See Discussion below for details.

7.3 Photodegradation on Soil (161-3)

Two studies which utilized similar materials and methods were submitted and reviewed. Neither study is acceptable because of the following common problems: (a) the intensity of the light source was reported to be three times greater than natural sunlight at 290-400 nm; (b) time zero samples were not collected; and (c) treated soil plates were incubated at elevated temperatures prior to irradiation. A new study is needed to assess the photodegradation of thidiazuron on soil.

7.4 Aerobic Soil Metabolism (162-1)

The study submitted is acceptable and partially fulfills the data requirement.

In a 361-day study conducted in a German sandy loam soil incubated aerobically in darkness at 21°C, phenyl-labeled thidiazuron (nominal concentration 0.3 ppm) degraded with a half-life of 111 days. The

principal compound identified throughout the study was parent thidiazuron1; three degradates were identified and detected in very small quantities (≤0.002 ppm). At the end of the study, bound residues and $^{14}CO_2$ accounted for 44.7 and 21.2% of the applied radioactivity, respectively.

The study did not address the aerobic soil metabolism of the thiadiazol moiety of the parent compound. To fulfill the data requirement, acceptable aerobic soil metabolism data are required for thiadiazol-labeled thidiazuron. See DER for details.

7.5 Anaerobic Soil Metabolism (162-2)

The study submitted is acceptable and fulfills the data requirement. No additional anaerobic soil metabolism data are required for thidiazuron at this time.

Following 30 days of aerobic incubation, thidiazuron (nominal concentration 0.3 ppm) was incubated anaerobically in a German sandy loam soil in darkness at 21°C for 90 days. During the anaerobic phase, thidiazuron degraded with a half-life of >90 days (the extrapolated half-life was 410 days). The degradate N-m-hydroxyphenyl-N'-(1,2,3-thiadiazol-5-yl)urea was detected at 0.003 ppm, which was the highest concentration of any identified degradate during the anaerobic incubation period. By the end of the study, 31.6% of the applied radioactivity was present in bound residues and $^{14}CO_2$ accounted for 1.8%, virtually all of which had evolved during the aerobic phase.

7.6 Leaching and Adsorption/Desorption (163-1)

The study submitted is acceptable and partially fulfills the data requirement.

Thiadiazol-labeled thidiazuron was slightly mobile to relatively immobile in non-U.S. soils classified as sand, loamy sand, sandy loam, and sandy clay loam soils. Respective Freundlich $K_{ads}$ values for these soils were 4.36, 16.2, 7.33, and 18.78. Adsorption increased with increasing soil organic carbon content and CEC.

To fulfill the data requirement, information is needed on the mobility of phenyl- and thiadiazol-labeled [$^{14}$C]thidiazuron residues aged aerobically for 30 days or one half-life (whichever is shorter) prior to leaching.

7.7 Terrestrial Field Dissipation (164-1)

The study submitted provides supplemental information regarding the terrestrial field dissipation of thidiazuron.

Thidiazuron did not dissipate from the upper 8 cm (3.1 inches) of a bare ground plot of sandy loam soil in Florida in the 9 months following the second of two applications (7-day interval) of thidiazuron (Dropp 50% WP) at 0.3 lb a.i./A. Minimal leaching of thidiazuron was reported. Small

quantities of the degradates photothidiazuron [1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea and thidiazolylurea were detected during the study.

The study cannot be used to fulfill the data requirement because: (a) its duration was insufficient (9 months) to assess a pattern of decline of the test substance; and (b) soil characteristics, field testing data (including meteorology), and plot maintenance practices were not reported adequately. Because the study was terminated before the dissipation of thidiazuron could be assessed under field use conditions, new field dissipation data are needed. Acceptable data from two sites in the U.S. where cotton is cultivated are needed to fulfill the data requirement.

7.8 Confined Accumulation in Rotational Crops (165-1)

Two studies and an appendix to one of the studies were reviewed which provide supplemental information regarding the uptake of thidiazuron by confined rotational crops. In the studies reviewed, $^{14}C$-residues accumulated in crops grown in soil treated earlier with thidiazuron (0.2 ppm) radiolabeled in two parts (the phenyl and thiadiazol moieties) of the compound. Accumulation generally decreased as the length of the rotational interval increased.

In Study 8 (MRID nos. 00030793 and 41364907) crops were planted 2 weeks or 6 months following treatment with thidiazuron. For soybeans planted 2 weeks after soil treatment, the reported $^{14}C$-residue levels (in parent equivalents) for both radiolabeled groups were <0.01-0.16 ppm in all plant parts. Residues in the 6-month rotational interval were ≤0.07 ppm for all soybean plant parts. In sugarbeets residue levels were ≤0.07 ppm and ≤0.01 ppm for the 2 week and 6 month groups, respectively. Total residues in sorghum leaves, stems, and fruit (2-week group) were ≤0.01 ppm; in roots, total residues were 0.01-0.09 ppm. For the 6 month group residues in sorghum plants were ≤0.01-0.03 ppm in mature leaves, stems and roots. In mature sorghum grain, residues of 0.05-0.13 ppm were detected.

In Study 9 (MRID no. 41364908) $^{14}C$-residues accumulated in sugarbeets, sorghum, and soybeans planted 197 days (sugarbeets and sorghum), 306 days (soybeans), and 398 days (all crops) after loamy sand soil was treated with phenyl- or thiadiazol-labeled $^{14}C$-thidiazuron at 0.2 ppm. Accumulation decreased as the length of the rotation increased. In soybeans residue levels were ≤0.01-0.11 ppm in stems, fruit, and roots for all planting intervals and both label positions. In sugarbeets, residues were ≤0.01-0.04 ppm in tops and roots; and in sorghum stems, grain, and roots residue levels were ≤0.01-0.08 ppm.

The studies cannot be used to fulfill the data requirement for the following reasons: (a) soils had high organic matter contents (3.4-3.8%) which are not typical of U.S. cotton soils and may have bound thidiazuron and inhibited residue uptake by crops; (b) $^{14}C$-residues in the crops and soil were not identified; (c) storage stability data were not provided for the plant and soil substrates; and (d) insufficient data were presented concerning the conditions under which the study was conducted.

It appears that new data are required. Because thidiazuron is used exclusively as a cotton defoliant, the new study should be conducted in U.S soils typical of cotton production and should incorporate rotational intervals and crops associated with cotton cultivation.

7.9 Accumulation in Fish (165-4)

The registrant (NOR-AM) has requested a waiver of this data requirement based on the low octanol/water partition coefficient and because the estimated environmental concentration (<4 ppb) is low in comparison to the aquatic $LC_{50}$ value for daphnid (10 ppb).

The octanol/water partition coefficient ($K_{ow}$) reported by NOR-AM to the Product Manager (but not validated by HED/Product Chemistry), 58.3 (log $K_{ow}$ = 1.77), indicates that thidiazuron has low potential to bioaccumulate in fish. Accordingly, EFGWB agrees to waive the accumulation in fish data requirement (165-4) at this time provided that the $K_{ow}$ is valid and that Ecological Effects Branch does not need this information.

7.10 Environmental Fate Summary

There are insufficient data for a comprehensive environmental fate assessment for thidiazuron at this time. Preliminary data indicate that mineralization to $CO_2$ and adsorption to soil may be major routes of dissipation. These data, however, were derived from European soils which are not representative of the compound's typical use sites (i.e. U.S. cotton soils). Additional data from U.S. cotton soils are needed to assess fully the environmental fate of thidiazuron. The following assessment is based on all available information.

An acceptable study indicates that thidiazuron is stable to hydrolysis at pH 5, 7, and 9. Supplemental studies indicate that it photodegrades rapidly in water and on soil ($t_{\frac{1}{2}}$ = <1 hr). The principal soil photodegradation product was the isomer 1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea. In an aerobic soil metabolism study conducted in a German sandy loam which partially fulfilled the data requirement, thidiazuron metabolized with a half-life of 111 days. At the end of the 1-year study, $^{14}CO_2$ and bound residues comprised 21.2% and 44.7% of the applied radioactivity, respectively, indicating that mineralization to $CO_2$ and adsorption to soil may be routes of dissipation. Data regarding the formation and decline of degradation products containing the thiadiazol moiety are needed to understand more completely the aerobic soil metabolism of the compound. Thidiazuron was stable in an acceptable anaerobic soil metabolism ($t_{\frac{1}{2}}$ = >>90 days). It was slightly mobile to relatively immobile in acceptable batch equilibrium studies ($K_{ads}$ were 4.36, 16.2, 7.33, and 18.78 on sand, loamy sand, sandy loam, and clay loam soils, respectively); adsorption was related to soil organic matter content and cation exchange capacity. Aged leaching data are needed to assess the mobility of degradation products. In a supplemental study conducted for 9 months, thidiazuron did not dissipate from the upper 8 cm of a Florida sand and did not leach significantly (low concentrations of parent were detected at 15-30 cm; it was not detected deeper than 30 cm). In two supplemental

studies, small amounts of thidiazuron accumulated in confined rotational crops.

8.0 RECOMMENDATIONS:

The only environmental fate data requirements fulfilled at this time are hydrolysis (161-1) and anaerobic soil metabolism (162-2). The aerobic soil metabolism (162-1) and leaching and adsorption/desorption (163-1) data requirements are partially fulfilled.

Several of the studies submitted were carried out using European soils, but thidiazuron is used exclusively as a cotton defoliant. Data from laboratory and field studies which use U.S. cotton soils are essential if an accurate environmental fate assessment is to be made. Moreover, additional key information is needed from laboratory studies to identify potential routes of dissipation and to provide inputs for modeling scenarios from which exposure and risk assessments will be made.

Acceptable terrestrial field dissipation data would provide accurate information on the route(s) of dissipation of thidiazuron under field-use conditions. It would supply field half-lives (which may differ from those observed in the laboratory) at multiple use sites, track the pattern of formation and decline in degradate concentration, and estimate the mobility of thidiazuron and its degradates under actual use conditions.

EFGWB believes that the fulfillment of all data requirements as indicated below will enable a thorough assessment of the environmental fate of thidiazuron and its degradation products under actual field use conditions.

8.2 Status of Environmental Fate Data Requirements

The status of the environmental fate data requirements for thidiazuron for terrestrial food crop use is summarized below:

| Environmental Fate Data Requirements | Status | MRID Number |
|---|---|---|
| **Degradation** | | |
| 161-1 Hydrolysis | Fulfilled (AWJ 04/28/93) | 42069203 |
| 161-2 Photodegradation in water | Not Fulfilled (JAH 12/06/89; AWJ 04/28/93) | 41188201<br>41364910 |
| 161-3 Photodegradation on soil | Not Fulfilled (AWJ 04/28/93) | 41364902<br>00156241 |
| 161-4 Photodegradation in air | Not Submitted | |

| Environmental Fate Data Requirements | | Status | MRID Number |
|---|---|---|---|
| **Metabolism** | | | |
| 162-1 | Aerobic soil | Partially Fulfilled (AWJ 04/28/93) | 41950101 |
| 162-2 | Anaerobic soil | Fulfilled (AWJ 03/04/93) | 41945201 |
| 162-3 | Anaerobic aquatic | Not Submitted | |
| **Mobility** | | | |
| 163-1 | Leaching, Adsorption/ Desorption | Partially Fulfilled (AWJ 04/28/93) | 41364909 |
| 163-2 | Volatility-lab | Not Submitted[1] | |
| 163-3 | Volatility-field | Not Submitted[1] | |
| **Dissipation** | | | |
| 164-1 | Soil | Not Fulfilled (AWJ 04/28/93) | 41761105 |
| 164-5 | Soil, long-term | Reserved[2] | |
| **Accumulation** | | | |
| 165-1 | Confined rotational crops | Not Fulfilled (AWJ 04/28/93) | 00030793 41364907 41364908 |
| 165-4 | Fish | Waived[3] | |
| **Spray Drift** | | | |
| 201-1 | Droplet size spectrum | Not submitted[4] | |
| 202-1 | Drift field evaluation | Not submitted[4] | |

[1] Based on the vapor pressure reported in EFGWB 's One-Liner Database (3 x $10^{-11}$ mm Hg), volatility does not appear to be an important route of dissipation. Therefore, this study is not required at this time.

[2] The long-term soil dissipation study (164-5) is reserved until evaluation of an acceptable soil dissipation study (164-1).

[3] The reported octanol/water partition coefficient ($K_{ow}$), 58.3 (log $K_{ow}$ = 1.77), indicates that thidiazuron has low potential to bioaccumulate in fish. Therefore, EFGWB agrees to waive the accumulation in fish data requirement (165-4) at this time provided that the $K_{ow}$ is validated and that Ecological Effects Branch does not need this information.

[4] This study is required when aerial applications (rotary and fixed wing) and mist blower or other methods of ground application are proposed and it is estimated that the detrimental effect level of those nontarget

organisms expected to be present would be exceeded. These data are required for all herbicides which are applied aerially.

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9.0 BACKGROUND:

Thidiazuron (trade name "Dropp"), a cotton defoliant used to remove leaves prior to harvest, is formulated as a 50% wettable powder. It may be applied by ground or air equipment at least 5 days prior to the anticipated harvest date. The maximum single application rate is 0.4 lb of formulated product per acre (0.2 lb a.i./A). Two applications may be made but the total applied should not exceed 0.6 lb formulated product per acre (0.3 lb a.i./A).

10.0 DISCUSSION:

10.1 See DERs for details of studies on hydrolysis (161-1), photodegradation on soil (161-3), aerobic and anaerobic soil metabolism (162-1 & 162-2), leaching and adsorption/desorption (163-1), terrestrial field dissipation (164-1), and accumulation in confined rotational crops (165-1).

10.2 MRID no. 41364910 - Supplement to Aqueous Photolysis Study (161-2)

The original aqueous photolysis study was reviewed on 12/06/89 (EFGWB no. 90737). A copy of the DER is attached. The purpose of this supplement was to characterize one of the photodegradates which was detected in the original study.

EFGWB concluded that the original study could not be used to fulfill the data requirement because: (1) the mercury arc lamp used did not have a continuous spectral distribution and the light intensity was more than three times that of natural sunlight; (2) different light sources were used in the photolysis rate and photodegradate identification studies; and (3) photodegradates were not characterized. The supplement addressed only the characterization of photodegradates.

In the original aqueous photolysis study, two photodegradates were detected. These compounds were assigned to HPLC peaks 1 and 3. According to the EFGWB review of 12/06/89 neither degradate was adequately characterized. The registrant's supplement indicates that the degradate assigned to peak 3 in the original study is the "rearrangement product" (i.e. isomer) of parent thidiazuron. The registrant refers to this compound as ZK 79 173. According to the registrant only the degradate assigned to peak 1, the main photoproduct at pH 7 and 9, was inadequately characterized.

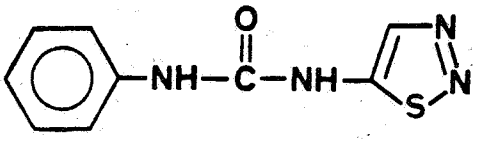
To identify this compound, thidiazuron was dissolved in 0.1 M NaOH and irradiated for 166 hr at 18-22°C. The photolysis solution was extracted with $CHCl_3$, acidified with 1M HCl, and extracted with diethylether. Extracts were combined and dried with $NaSO_4$, filtered, and solvent was evaporated until a precipitate was formed. The supernatant was decanted and the residue washed with cold diethylether to yield a light yellow

solid. This product was analyzed structurally by $^{1}H$-NMR, $^{13}C$-NMR, IR, and MS and found to be 1-cyano-3-phenylurea. The identity of the photoproduct also was confirmed by comparing the HPLC chromatogram of a standard solution of 1-cyano-3-phenylurea with the chromatogram of peak 1 in the original photodegradation study.

Although the photodegradate assigned to peak 1 in the original study has been identified as 1-cyano-3-phenylurea, the deficiencies outlined in the EFGWB review of 12/06/89 remain (see Conclusions and Background above). A new aqueous photolysis study is needed.

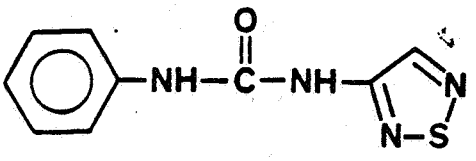
11.0 COMPLETION OF ONE-LINER: Updated one-liner attached.

12.0 CBI APPENDIX: N/A



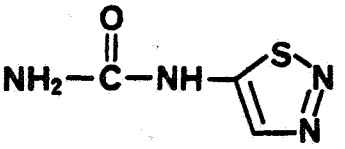
1-Phenyl-3-(1,2,3-thiadiazol-5-yl)urea

(Thidiazuron)

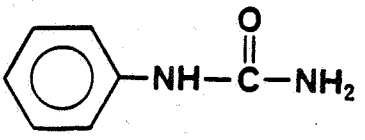


1-Phenyl-3-(1,2,5-thiadiazol-3-yl)urea (Photoproduct I; Study 1)

Photothidiazuron (ZK 80 178; Study 3)



Thidiazolylurea (ZK 85 290)




Phenylurea (ZK 44 483)

DATA EVALUATION RECORD

STUDY 1

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CHEM 120301 Thidiazuron §161-1

FORMULATION--00--ACTIVE INGREDIENT

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STUDY ID 42069203
Tschampel, M. 1991. The determination of the rate of hydrolysis of thidiazuron. Unpublished study performed by Schering AG, Berlin, Federal Republic of Germany, and submitted by NOR-AM Chemical Co. Laboratory project ID APC 71/91

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Date: 28 APR 1993

APPROVED BY:

Paul J. Mastradone, Ph.D.
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OPP/EFED/EFGWB

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Date: [illegible] APR 1993

CONCLUSIONS:

Degradation - Hydrolysis

1. This study is acceptable and fulfills the hydrolysis data requirement for thidiazuron.

2. In a 36-day study, no hydrolysis of thidiazuron (nominal concentration of 10 ppm) was reported in aqueous buffer solutions (pH 5, 7, and 9) held in darkness at 25 ± 1°C. EFGWB concludes that thidiazuron is stable to hydrolysis at pH 5, 7, and 9.

3. No further hydrolysis data for thidiazuron are required at this time.

MATERIALS AND METHODS:

Stock solutions were prepared by adding 20.53 mg of thidiazuron (99.4% pure) to 20 mL $CH_3CN$. Sterile buffer stock solutions at pH 5, 7, and 9 were prepared using 0.1 M acetate, phosphate, and borate, respectively. One mL of stock solution was added to 20 mL of each of the buffered stock solutions and 75 mL of double distilled water. The volume was brought to 100 mL with double distilled water to yield a test solution concentration of ≈ 10 mg/L with 1% $CH_3CN$. The three test solutions were placed into two vials for each sampling period and held in darkness at 25 ± 1°C for 855 hr (35.6 days).

At time zero and at 17, 41, 83, 180, 371, 707, & 855 hr two 200-$\mu$L aliquots were removed from each vial and analyzed by HPLC. The pH of each test solution also was measured at each sampling interval. HPLC peaks of test solutions were compared with standard solutions of thidiazuron and potential degradates.

DATA SUMMARY:

Table 1 shows the pH, mean thidiazuron concentration, and percent of initial concentration for each sampling interval. For the pH 5 test solution, thidiazuron concentrations were 9.94-10.29 mg/L and the measured pH was 5.05-5.09. Thidiazuron comprised 97.9-101.4% of the time zero concentration throughout the experiment. For the pH 7 test solution, thidiazuron concentrations were 10.06-10.40 mg/L (98.9-102.3% of the time zero concentration); the measured pH was 7.21-7.23. For the pH 9 solution, thidiazuron concentrations were 9.76-10.34 mg/L (97.2-103.0% of the time zero concentration) and the measured pH was 9.07-9.09.

DISCUSSION:

1. EFGWB prefers that laboratory studies be conducted using radiolabeled active ingredient to facilitate compound identification and mass balance calculation. For this study, however, the "cold" method was adequate because thidiazuron was stable and good mass balance was achieved.

2. The aqueous solubility of thidiazuron was reported as 31 mg/L, yet test solutions contained 1% $CH_3CN$. EFGWB prefers that cosolvents not be used unless they are required to get the test substance into solution.

3. It is possible that hydrolysis was occurring very slowly in the pH 9 buffer solution. For the seven sampling intervals following time zero, thidiazuron concentrations were 100.2-103.0% of the time zero concentration (Table 1). At 855 hr, the thidiazuron concentration was 97.2% of the time zero concentration.

EFGWB THIDIAZURON REVIEW

Page_____ is not included in this copy.

Pages 27 through 30 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

X FIFRA registration data.

____ The document is a duplicate of page(s) _____.

____ The document is not responsive to the request.

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

DATA EVALUATION RECORD

STUDY 2

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CHEM 120301 Thidiazuron §161-3

FORMULATION--00--ACTIVE INGREDIENT

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STUDY ID 41364902
Klehr, M., J. Iwan, and J. Riemann. 1983. W23 Thidiazuron: An experimental approach to the photolysis of pesticides adsorbed on soil: Thidiazuron. Pesticide Science 14:359-366. Published study performed by Schering AG, Berlin, Germany, and submitted by Nor-Am Chemical Company, Wilmington, DE.

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DIRECT REVIEW TIME = 8

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28 APR 1993

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study is unacceptable and cannot be used to fulfill the data requirement for the following reasons:

   (a) The intensity of the light source at sample distance was reported to be three times greater than natural sunlight at 290-400 nm.

   (b) Time zero samples were not collected.

   (c) Treated soil plates were incubated at 60°C for approximately 1 hr prior to irradiation.

   (d) After remaining relatively stable initially, material balances decreased abruptly at the final sampling interval.

2. The problems with this study cannot be resolved with the submission of additional data. A new study must be submitted.

METHODOLOGY:

A glass plate (20 x 20 cm) was coated with a 0.5-mm layer of sandy loam soil (0.69% organic carbon, pH 5.5) according to the method of Helling. Thiadiazol-labeled [5-$^{14}$C]thidiazuron (radiochemical purity >97%, specific activity 2.0 mCi/mMol, Schering AG), dissolved in methanol, was applied at 1.5 ug/cm$^2$ (150 g/ha) to thirty 3- x 4-cm regions on the plate using a thin-layer spotter. The treated soil plate was heated at 60°C for 1 hour, then incubated at 20°C for approximately 7 days. After the 7 day incubation and prior to irradiation, fifteen of the regions on the plate were covered with aluminum foil to serve as dark controls. The treated soil plate was placed in a ventilated box that was sealed with a WG 295 glass filter plate; the soil plate rested on a circulating water cooling system that maintained the soil temperature at ≤30°C (Figure 4). Air was drawn (flow rate unspecified) through the photolysis box, then sequentially through 2-aminoethanol (three traps) and ethane-1,2-diol (one trap) trapping solutions. The treated soil plate was continuously irradiated using a xenon arc lamp equipped with a solarized Duran filter; the Duran filter in combination with the WG 295 glass filter eliminated radiation below 290 nm (Figure 2). The intensity of the light source at sample distance (28 cm) was 13.5 mW/cm$^2$ at wavelengths 290-400 nm; it was reported that the intensity of the xenon lamp was three times greater than natural sunlight at 290-400 nm (4.4 mW/cm$^2$ at noon in summer, latitude 50 N). Three irradiated and dark control regions were scraped from the soil plate after 0.25, 0.5, 1.0, 2.0, 3.75, and 18.0 hours of irradiation; sampling intervals for the trapping solutions were not reported.

Soil samples were extracted three times with methanol:acetone (1:1, v:v); extracts were separated from the soil by centrifugation, decanted, and combined. Aliquots (50 uL) of the extract were analyzed for total radioactivity using LSC. Additional aliquots (200 uL) were analyzed using one-dimensional TLC on silica gel plates developed in hexane:methylene chloride:ethyl acetate:methanol (40:30:25:5, v:v:v:v) or two-dimensional TLC using hexane:methylene chloride:ethyl acetate:methanol followed by ethyl acetate. Radioactive areas were detected using a TLC scanner or autoradiography and quantified by LSC after scraping the silica gel from the plate; identification was made by comparison with unlabeled reference standards cochromatographed with the samples. Additional aliquots were analyzed using reverse-phase HPLC with a mobile phase of methanol:water (1:1, v:v); fractions were collected (time interval unspecified) and analyzed for total radioactivity using LSC. Unextracted [$^{14}$C]residues remaining in the extracted soil were quantified using LSC following combustion.

Aliquots of the trapping solutions were analyzed for total radioactivity using LSC.

DATA SUMMARY:

Thiadjazol-labeled [5-$^{14}$C]thidiazuron (radiochemical purity >97%), at 1.5 ug/cm$^2$ (150 g/ha), isomerized rapidly (observed half-life <0.5 hour) on sandy loam soil that was continuously irradiated with a dual-filtered (WG

295 glass and solarized Duran) xenon arc lamp (intensity 13.5 mW/cm$^2$ at 290-400 nm) at ≤30°C for 18 hours after a preincubation period of approximately 7 days in the dark. At wavelengths between 290-400 nm, the intensity of the xenon lamp was reported to be three times greater than noontime summer sunlight at latitude 50°N. In contrast, [14C]thidiazuron isomerized with an observed half-life of >7 days on sandy loam soil incubated in the dark. The only photoproduct identified in the irradiated soil was

the isomer 1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea (photoproduct I).

In extracts of soil that had been irradiated for 18 hours following 7 days of dark incubation, thidiazuron comprised 19.5% of the applied radioactivity, its isomer 1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea comprised 9.5% (maximum 36.7% at 2 hours), approximately five unidentified polar [14C]-compounds comprised a total of 12.6%, and unextracted [14C]residues comprised 28.4%; no [14C]volatiles were detected in the trapping solutions (Tables 1 and 2). In extracts from soil that had been incubated in the dark for approximately 7.75 days after treatment, thidiazuron was the only compound detected and comprised 67.2% of the applied radioactivity. During the study, material balances ranged from 76.8 to 93.3% of the applied (Table 1).

DISCUSSION:

1. The intensity of the light source at sample distance (28 cm), 13.5 mW/cm$^2$ at wavelengths 290-400 nm, was reported to be three times greater than natural sunlight at 290-400 nm (4.4 mW/cm$^2$ at noon in summer, latitude 50°N). One of the main objectives of the study is to determine whether photodegradation on soil is a route of dissipation. The use of a light intensity which is substantially greater than what would be encountered naturally could easily overestimate the importance of photodegradation on soil as a route of dissipation. A new study which uses natural or simulated sunlight should be submitted. The new study should also address the other problems identified in this review.

2. The following aspects of the experimental design were not appropriate to accurately assess the photodegradation of thidiazuron on soil:

   (a) Following application of the test substance, the plates were heated at 60°C for 1 hr, then incubated at 20°C for approximately 7 days. Apparently the test system was incubated after pesticide application and prior to irradiation to dry the soil.

   (b) Immediate posttreatment soil samples were not taken, and the actual posttreatment sampling intervals could not be determined.

   (c) The sampling intervals for both the irradiated and dark control samples were reported by the study authors in terms of hours of irradiation and did not take into account the preincubation period. At the first sampling interval (after 0.25 hours of irradiation and approximately 7 days of preincubation), parent thidiazuron comprised

an average 56.4% of the applied radioactivity in the irradiated soil extracts and 83.4% in the dark control soil extracts.

The photodegradation on soil study should be designed to assess the effects of natural or simulated sunlight on a pesticide applied to a viable soil. Samples should be taken at time zero to confirm application rate and irradiation should begin immediately after application. The procedures used interfered with the ability to assess photodegradation on a viable soil.

3. Isomerization of thidiazuron in the dark controls appeared to be accelerated (possibly by increased temperature) when incubated in the photolysis box. An average 16.6% of the applied thidiazuron isomerized to 1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea during the 7-day preincubation period, but an additional 16.2% of the parent compound isomerized after only 18 hours in the photolysis box.

4. Material balances were incomplete at the final sampling interval; 23.2% of the theoretical applied radioactivity in the irradiated soil samples was unaccounted for after 7 days of preincubation and 18 hours of irradiation, and 16.1% of the applied in the dark controls was unaccounted for at the same sampling interval. At the first sampling interval (0.25 hours postirradiation), approximately 10% of the applied was unaccounted for in both the irradiated and dark control soil samples. The study authors suggested that the missing radioactivity was lost during application but did not provide evidence to support their claim. Since time 0 samples were not collected and the treated soil plates were preincubated for approximately 7 days, it is uncertain when the radioactivity was lost. Material balances were relatively stable during the initial five sampling intervals, ranging from 88.0 to 93.3% of the applied, then abruptly decreased at the final (sixth) sampling interval. Samples were collected after 0.25, 0.5, 1.0, 2.0, 3.75, and 18.0 hours of irradiation. It is possible that if samples had been collected at least once between the 3.75- and 18.0-hour intervals, sufficient information may have been available to adequately interpret the data.

5. The study authors failed to account for all of the extracted radioactivity. Following analysis of the soil extracts, up to an average 35.2% of the applied radioactivity was unaccounted for in the irradiated soil extracts and up to an average 19.7% was unaccounted for in the dark control soil extracts.

6. The photodegradation on soil study should be conducted on the same soil as the aerobic soil metabolism study. Acceptable aerobic soil metabolism still must be submitted. Both soil photolysis and aerobic soil metabolism studies should be performed on a typical U.S. cotton soil.

7. The study authors classified the photoproduct 1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea as a degradate of thidiazuron; however, the compound is actually an isomer of the parent test substance.

8. The sandy loam classification of the German soil could not be confirmed. The particle size scale used was not equivalent to the USDA scale; the sand fraction contained both sand and silt particles. The grain size distribution reported by the study authors was 0.02-0.2 mm - 61%; 0.002-0.02 mm - 26%; and <0.002 mm - 13%. The CEC of the soil was not reported.

9. The average incubation temperature and/or the temperature range were not reported. It was only reported that the soil temperature did not exceed 30°C during irradiation of the soil plate.

10. It was not specified how many soil plates were actually treated and irradiated. There were 30 treated regions (15 irradiated and 15 dark controls) on a soil plate and six (three irradiated and three dark controls) were scraped from the plate at each sampling interval. This would allow for five sampling intervals, but there was a total of six sampling intervals. Therefore, more than one soil plate must have been prepared and irradiated, but it could not be determined how many. Also, the photolysis box was only large enough to hold one plate.

11. Following TLC of the soil extracts, it was not specified how the unlabeled reference standards were visualized.

12. After averaging the percent of applied thidiazuron recovered in the dark control soil extracts and using that value as a time 0 for the irradiated samples, the study authors calculated a photodegradation half-life of 0.5 hours for thidiazuron (Figure 7).

13. The complete wavelength distribution and total irradiant intensity of the xenon light source were not compared to natural sunlight; comparisons were only made at wavelengths of 290-400 nm. The study authors reported the spectral distribution and intensity up to 400 nm because the majority of pesticides absorb at wavelengths <400 nm; however, the specific absorption spectrum of thidiazuron was not reported.

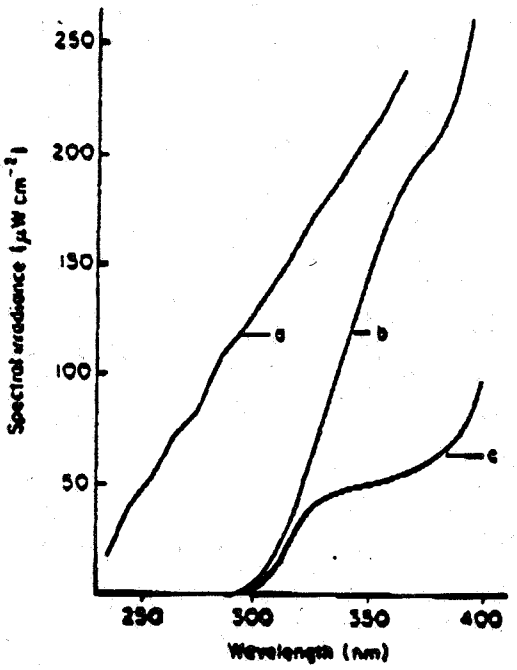


**Figure 2.** Spectral irradiance: (a) XBF 2500 W/1, unfiltered; (b) XBF 2500 W/1, Duran+WG 295 filter; (c) natural sunlight at latitude 50° N.[7]

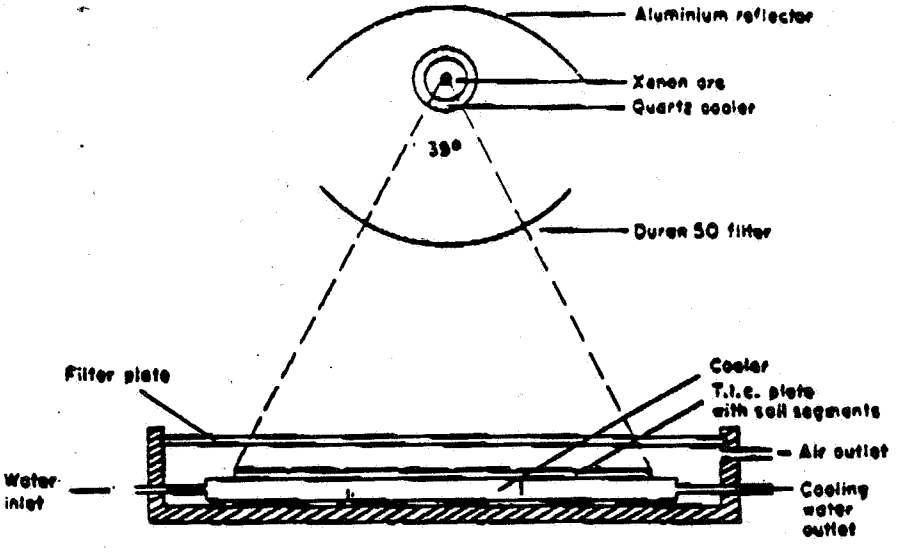


**Figure 4.** Equipment for photolysis studies with pesticides adsorbed on soil.

STUDY AUTHOR(S)'S RESULTS AND/OR CONCLUSIONS

(INCLUDING PERTINENT TABLES AND FIGURES)

## 3. Results and discussion

### 3.1. Material balances

Material balances are given in Table 1. As the recovery of thidiazuron from soil without irradiation was 90.3% (s.d. = 2.1%, $n = 3$) due to losses during the spraying procedure, the material balance had to be corrected for this value. In the bottles containing 2-aminoethanol and ethane-1,2-diol, no radioactivity was found.

The results given in Table 1 show that, in all experiments, about 10% of the original amount of radioactivity was lost during spraying. The remaining 90% was recovered from the irradiated,

Table 1. Material balances, after irradiation, of thidiazuron applied to soil surfaces

| Irradiation time (h) | Irradiated (+) or non-irradiated (−) | Extracted radioactivity[a] (%) (s.d.) | Difficult-to-extract radioactivity[a] (%) (s.d.) | Total radioactivity extracted[a] (%) (s.d.) | Total radioactivity extracted (corrected for recovery) (%) |
|---|---|---|---|---|---|
| 0.25 | + | 85.8 (1.5) | 6.3 (0.5) | 92.1 (1.2) | 101.9 |
| | − | 86.9 (0.4) | 4.5 (0.9) | 91.4 (0.6) | 101.1 |
| 0.5 | + | 81.5 (3.0) | 8.5 (0.4) | 90.0 (2.9) | 99.7 |
| | − | 84.0 (1.2) | 7.7 (1.3) | 91.7 (0.9) | 101.6 |
| 1.0 | + | 76.9 (2.9) | 14.5 (1.5) | 91.4 (1.4) | 101.2 |
| | − | 84.2 (0.7) | 9.1 (0.7) | 93.3 (0.5) | 103.3 |
| 2.0 | + | 74.6 (0.4) | 13.4 (1.0) | 88.0 (0.7) | 97.5 |
| | − | 81.9 (0.5) | 8.2 (1.7) | 90.1 (1.7) | 99.8 |
| 3.75 | + | 68.3 (1.0) | 21.7 (0.9) | 90.1 (1.0) | 99.8 |
| | − | 80.5 (2.0) | 11.1 (1.3) | 91.6 (1.0) | 101.4 |
| 18.0 | + | 47.5 (0.5) | 28.4 (3.0) | 76.8 (3.0) | 85.0 |
| | − | 73.7 (3.0) | 10.1 (2.1) | 83.9 (1.5) | 92.9 |

[a] The percentages given are of the applied dose, and are the averages of three segments each; $n = 3$).

as well as from the non-irradiated segments. Additionally, it can be seen that the recovered radioactivity is constant with a small standard deviation in each group of segments, at each time-interval and in all experiments.

### 3.2. Characterisation of the conversion products

To identify the conversion products of thidiazuron, extracts of the irradiated soil segments were co-chromatographed with thidiazuron and a known photoproduct 1-Phenyl-3-(1,2,5-thiadiazol-3-yl)urea (I; Figure 6), formed by the photolysis of thidiazuron in aqueous solution.[11] Two-dimensional t.l.c. was used [solvent system 1: hexane + dichloromethane + ethylacetate + methanol (40 + 30 + 25 + 5 by volume); solvent system 2: ethylacetate; plates: Silica gel F60 (E. Merck)].

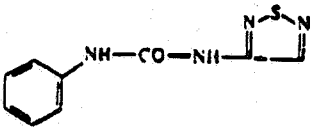


Figure 6. The known photoproduct 1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea (I).

It was shown by autoradiography (Kodak X-ray film) that the radioactivity spots on the t.l.c. plates corresponded to thidiazuron and the known photoproduct I. One additional spot at the origin was also detected. This unknown polar compound did not move on the t.l.c. plates. The extracts of non-irradiated soil segments contained thidiazuron only.

Analysis of the extracts by h.p.l.c. confirmed these results and, additionally, indicated that the polar spots visible on the t.l.c. plates at the origin contained about five unknown polar compounds (compare Figure 5, fractions 6 to 24). These polar compounds, formed by photolysis, were not isolated and identified because the quantities were too small.

### 3.3. The kinetics of photoconversion

H.p.l.c. and t.l.c. analysis of the extracts of irradiated and non-irradiated soil segments served to determine the quantities of thidiazuron, the photoproduct (I), and the unknown polar compounds (sum) at each irradiation time interval. The results, given as percentages of the applied dose, are shown in Table 2. These data show that thidiazuron was rapidly photolysed on the irradiated soil segments, whereas it remained unchanged on the non-irradiated segments.

Table 2. Distribution of radioactivity as shown by the h.p.l.c. chromatograms of the extracts of irradiated soil segments; the peaks were correlated to authentic standard compounds

| Irradiation time (h) | Irradiated (+) or non-irradiated (−) | Thidiazuron[a] (%) (s.d.) | Photoproduct I[a] (%) (s.d.) | Polar products[a] (%) (s.d.) |
|---|---|---|---|---|
| 0.25 | + | 56.4 (1.8) | 22.5 (0.9) | 2.2 (0.1) |
| | − | 83.4 (0.3) | — | — |
| 0.5 | + | 42.8 (2.0) | 27.9 (0.3) | 4.0 (0.3) |
| | − | 76.8 (0.3) | — | — |
| 1 | + | 35.7 (1.4) | 27.0 (0.9) | 6.4 (0.3) |
| | − | 73.7 (0.2) | — | — |
| 2 | + | 23.8 (0.7) | 36.7 (0.6) | 9.5 (0.5) |
| | − | 78.2 (1.0) | — | — |
| 3.75 | + | 25.0 (1.2) | 25.6 (0.9) | 4.8 (0.5) |
| | − | 71.9 (1.1) | — | — |
| 18.0 | + | 19.5 (2.4) | 9.5 (1.1) | 12.6 (1.5) |
| | − | 67.2 (3.2) | — | — |

[a] The percentages given are of the applied dose; $n = 3$ in all cases. The average of the non-irradiated segments is 79.2% thidiazuron.

The quantities of unphotolysed thidiazuron recovered from the irradiated soil segments indicate that only about 80% of the applied dose was photolysed, whereas about 20% remained unphotolysed. This may have been due to penetration of about 20% of the applied solution into deeper soil layers impenetrable to sun light.

The disappearance of the accessible thidiazuron can be described approximately by first-order kinetics as shown in Figure 7. The average thidiazuron content of the non-irradiated segments was taken as the percentage present at time $t=0$. A digital computer simulation[12] of the reaction kinetics yielded a first-order reaction constant ($k$) = 1.42 $h^{-1}$ and a half-life ($t_{1/2}$) = 0.5 h.

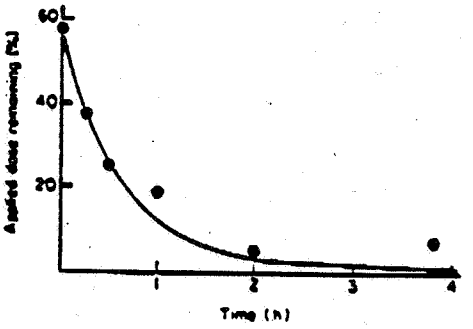


Figure 7. Disappearance with time, during irradiation, of [$^{14}$C]thidiazuron adsorbed on soil surfaces: the percentage of the applied dose remaining is reduced by the 20% that remains unphotolysed due to penetration into non-irradiated layers of the soil.

Additionally, the data given in Table 2 show that the photoproduct I which is formed is further converted to polar compounds by longer irradiation. This process is, however, much slower than formation of the original photoproduct.

The standard deviations of recoveries from identically treated soil segments show that the reproducibility of these values was quite good.

## 4. Conclusions

The method described to test the photodegradability of pesticides on soil surfaces provides a simple procedure for obtaining significant data, useful for estimating the persistence of a pesticide in the environment. The method is quite simple because all the samples can be applied to the soil segments in one single working process, and because all the segments are irradiated simultaneously. After scraping off the segments at various time intervals, only standard analytical methods are necessary for further processing, including the isolation of conversion products. The repeated use of standard operations makes this method suitable for routine measurements. The reliability of the method in terms of reproducibility can be checked by testing three irradiated and three non-irradiated samples at each time interval. Reliability in terms of accuracy can be checked by material balances.

The described technique of pesticide application to the soil surface is quite similar to spraying technique used in normal agricultural practice (spraying from an aeroplane or with other technical devices), with the restriction that in agricultural practice, formulations of pesticides are used. An additional advantage of this application technique is the reduced penetration of the pesticide into non-irradiated layers of the soil.

In short, the method described provides information on the products of photodegradation or photoconversion, on the potential side reactions in the adsorbed phase, and on the kinetics of photoreactions and potential side reactions. In the above case, a rapid photoconversion was observed, yielding a photoproduct known from aqueous photolysis experiments with thidiazuron.

## Acknowledgement

The authors gratefully acknowledge the skilled technical assistance of Mrs B. Paetzelt.

DATA EVALUATION RECORD

STUDY 3

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CHEM 120301 Thidiazuron §161-3

FORMULATION--00--ACTIVE INGREDIENT

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STUDY ID 00156241
Klehr, M., J. Iwan, and J. Riemann. 1981 Photodegradation of thidiazuron (SN 49537) on soil surfaces. Unpublished study performed by Schering AG, Berlin, Germany, and submitted by Nor-Am Chemical Company, Wilmington, DE.

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Date: 28 APR 1993

APPROVED BY:

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Date:

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study is unacceptable and cannot be used to fulfill the data requirement for the following reasons:

   (a) The intensity of the light source at sample distance was reported to be three times greater than natural sunlight at 290-400 nm.

   (b) Treated soil plates were incubated at 80°C for approximately 12 hr and stored at room temperature (50% relative humidity) for several weeks before irradiation.

   (c) Time zero samples were not collected.

2. The problems cannot be resolved with the submission of additional data from this study. A new study is needed to assess the photodegradation of thidiazuron on soil.

METHODOLOGY:

A glass plate (20 x 20 cm) was coated with a 0.5-mm layer of German standard soil 2.3 (sandy loam; 0.69% organic carbon, pH 5.5). Thiadiazol-labeled [5-$^{14}$C]thidiazuron (radiochemical purity >97%, specific activity 2.2 mCi/mMol, Schering AG), dissolved in methanol, was applied at 1.5

$\mu g/cm^2$ (150 g/ha) to thirty 3- x 4-cm regions on the plate using a thin-layer spotter. In separate experiments, $^{14}C$-phenyl-labeled thidiazuron (specific activity 2.0 $\mu Ci/mMol$) was used. The treated soil plate was dried at 80°C for 12 hr, then stored at room temperature at approx 50% relative humidity until use (typically several weeks). For each sampling interval, six soil segments were used (three were irradiated and three were covered with aluminum foil for dark controls). The treated soil plate was placed in a ventilated box that was sealed with a WG 295 glass filter plate; the soil plate rested on a circulating water cooling system that maintained the soil temperature at $\leq$30°C. To trap volatiles, air was drawn (flow rate unspecified) through the photolysis box, then sequentially through ethanolamine and ethylene glycol. The treated soil plate was continuously irradiated using a xenon arc lamp equipped with a solarized Duran filter; the Duran filter in combination with the WG 295 glass filter eliminated radiation below 290 nm. The intensity of the light source at sample distance (28 cm) was 13.5 $mW/cm^2$ at wavelengths 290-400 nm; it was reported that the intensity of the xenon lamp was three times greater than natural sunlight at 290-400 nm (4.4 $mW/cm^2$ at noon in summer, latitude 50°N). Three irradiated and dark control regions were scraped from the soil plate after 0.25, 0.5, 1.0, 2.0, 3.75, and 18.0 hours of irradiation; sampling intervals for the trapping solutions were not reported.

Soil samples were extracted three times with methanol:acetone (1:1, v:v); extracts were separated from the soil by centrifugation, decanted, and combined. Aliquots of the extract were analyzed for total radioactivity using LSC. Additional aliquots were analyzed using one-dimensional TLC on silica gel plates developed in hexane:dichloromethane:ethyl acetate:methanol (40:30:25:5, v:v:v:v) or two-dimensional TLC using hexane:methylene chloride:ethyl acetate:methanol followed by ethyl acetate. Radioactive areas were detected using a TLC scanner or autoradiography and quantified by LSC after scraping the silica gel from the plate; identification was made by comparison with unlabeled reference standards cochromatographed with the samples. Additional aliquots were analyzed using reverse-phase HPLC with a mobile phase of methanol:water (1:1, v:v); fractions were collected (time interval unspecified) and analyzed for total radioactivity using LSC. Unextracted [$^{14}C$]residues remaining in the extracted soil were quantified using LSC following combustion. Compound identification was made by comparison of HPLC retention times of standards and by two-dimensional TLC comparison with standards. Aliquots of the trapping solutions were analyzed for total radioactivity using LSC.

To assess recoveries, two replicates of each of the labeled materials were analyzed. Soil was treated with labeled thidiazuron as described above. Segments were scraped and extracted immediately, extracts were analyzed by LSC, and soils were combusted to determine unextractable radioactivity.

DATA SUMMARY:

In the recovery studies, an average of 82% of the applied radioactivity was recovered in extracts and 7.6% was recovered from combusted soil. The difference between the applied and recovered (9.7%) was assumed to be lost

while spraying stock solutions on soil samples. (This was verified in a separate study where 15 $\mu$L of thidiazuron stock solution was applied to clean glass plates. The recovery was 91% of the applied radioactivity.)

Table 3 shows the distribution of radioactivity in HPLC chromatograms for soil treated with thiadiazol-labeled [5-$^{14}$C]thidiazuron and dark controls. After 0.25 hr of irradiation, 56.4% of the applied radioactivity was present in parent thidiazuron (1-phenyl-3-[1,2,3-thiadiazol-5-yl urea], or SN 49537); 22.5% of the applied was in 1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea (SN 79173). The concentration of thidiazuron generally declined with increased irradiation time, and in samples irradiated for 18 hr, the respective concentrations were 19.5 and 9.5% of the applied radioactivity. In dark controls, parent thidiazuron declined from 83.4% at 0.25 hr to 67.2% after 18 hr of irradiation. SN 79173 was not detected in any dark controls. The concentration of unidentified polar photoproducts ranged from 0.4% of the applied (after 1 hr irradiation) to 12.6% after 18 hr irradiation. Nonextractable radioactivity (expressed as a percent of the radioactivity recovered from non-irradiated controls) ranged from 7.2% (0.25 hr) to 37.8% (18 hr). Material balances were 76.8-93.3% of the applied radioactivity; when corrected for a recovery of 91%, material balances were 85.0-103.3.%.

Table 7 shows the distribution of radioactivity in HPLC chromatograms for soil treated with 1-$^{14}$C-phenyl thidiazuron and dark controls. In irradiated samples, recovery of parent was highest after 0.25 hr of irradiation (43.8% of applied) and lowest after 1 hr of irradiation (24.5%). The lowest and highest reported concentrations of the photoproduct SN 79173 corresponded to the same periods with the respective concentrations being 16.7% and 25.4% of the applied, respectively. The concentration of unidentified polar compounds in irradiated soil samples increased from 2.9% of the applied radioactivity (0.25 hr) to 11.6% at the end of the experiment (4 hr). Nonextractable radioactivity (expressed as a percent of the radioactivity recovered from non-irradiated controls) ranged from 10.1% (0.25 hr) to 20.1% (4 hr). Material balances were 75.6-93.5% of the applied radioactivity; when corrected for recoveries, material balances were 80.8-103.5%.

The photolytic half-life of thidiazuron under the experimental conditions was reported to be <1 hr.

DISCUSSION:

1. The intensity of the light source was reported to be three times greater than natural sunlight at 290-400 nm at noon in summer at 50°N latitude. One of the main objectives of the study is to determine whether photodegradation on soil is a route of dissipation. The use of a light intensity which is substantially greater than what would be encountered naturally could easily overestimate the importance of photodegradation on soil as a route of dissipation. A new study which uses natural or simulated sunlight should be submitted. The new study should also address the other

problems identified in this review and should be conducted on a typical U.S. cotton soil.

2. The following aspects of the experimental design were not appropriate to accurately assess the photodegradation of thidiazuron on soil:

   (a) Following application of the test substance, the plates were heated at 80°C for approximately 12 hr and stored at room temperature (50% relative humidity) for several weeks before irradiation. Apparently the test system was incubated after pesticide application and prior to irradiation to dry the soil.

   (b) Immediate posttreatment soil samples were not taken, and the actual posttreatment sampling intervals could not be determined.

   (c) The sampling intervals for both the irradiated and dark control samples were reported by the study authors in terms of hours of irradiation and did not take into account the preincubation period. At the first sampling interval.

   The photodegradation on soil study should be designed to assess the effects of natural or simulated sunlight on a pesticide applied to a viable soil. Samples should be taken at time zero to confirm application rate and irradiation should begin immediately after application. The procedures interfered with the ability to assess photodegradation on a viable soil.

3. For phenyl-labeled thidiazuron, the pattern of decline of parent was not apparent (Table 7). After 0.25, 0.5, and 1 hr of irradiation, parent thidiazuron accounted for 43.8, 41.8, and 24.5% of the applied radioactivity, respectively. However, after 2 and 4 hr of irradiation, these concentrations were reported to be higher (30.0 and 31.4%, respectively) than after only 1 hr of irradiation. This apparent discrepancy coincides with the somewhat poor recoveries in all samples except the 4 hr irradiation period (which was the longest irradiation time in this experiment; see Table 6). The study states that "the reasons for the insufficient results in the other experiments are not yet clear."

4. The photodegradation on soil study should be conducted on the same soil as the aerobic soil metabolism study. Acceptable aerobic soil metabolism still must be submitted (see the DER for Study 4). Both soil photolysis and aerobic soil metabolism studies should be performed on a typical U.S. cotton soil.

5. The study authors classified the photoproduct 1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea as a degradate of thidiazuron. This compound is actually an isomer of the parent test substance.

6. The test soil was reported only as "standard soil 2.3 (sandy loam, particles < 300$\mu$m)." From the other photodegradation on soil study reviewed with this package (see DER for Study 2), standard soil was said

to have a pH of 5.5. The textural classification of this German soil could not be confirmed. The particle size scale used was not equivalent to the USDA scale; the sand fraction contained both sand and silt particles. The grain size distribution reported by the study authors was 0.02-0.2 mm - 61%; 0.002-0.02 mm - 26%; and <0.002 mm - 13%. The CEC of the soil was not reported. Because thidiazuron is used solely as a cotton defoliant, all studies should be carried out on typical U.S. cotton soils.

7. Nonextractable radioactivity and concentration of parent and photoproducts were in some cases expressed as a percent of the radioactivity recovered from non-irradiated controls (e.g. Table 4). It is not clear why these data were based on recovery of radioactivity from non-irradiated soil samples.

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DATA EVALUATION RECORD

STUDY 4

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CHEM 120301 Thidiazuron §162-1

FORMULATION--00--ACTIVE INGREDIENT

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STUDY ID 41950101
Feyerabend, M. 1991. Aerobic degradation of [UL-14C]-phenyl-thidiazuron in a sandy loam soil at 21°C. Unpublished study performed by Schering AG, Berlin, Federal Republic of Germany, and submitted by NOR-AM Chemical Co. Laboratory Project ID UPSR 21/91.

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Date: 6 APR 1993

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Date:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. The study is acceptable and partially fulfills the aerobic soil metabolism data requirement (162-1) for thidiazuron.

2. In a 361-day study conducted in a German sandy loam soil incubated aerobically in darkness at 21°C, phenyl-labeled thidiazuron (nominal concentration 0.3 ppm) degraded with a half-life of 111 days. The principal compound identified throughout the study was parent thidiazuron. Three identified degradates were detected in very small quantities (≤0.8% of the applied radioactivity [0.002 ppm]) and one unidentified polar degradate was present at a maximum of 1.6% of the applied (0.005 ppm). At the end of the study, bound residues represented 44.7% of the applied radioactivity and $^{14}CO_2$ accounted for 21.2%.

3. To completely fulfill the data requirement, acceptable aerobic soil metabolism data are required for thiadiazol-labeled thidiazuron. The study should be conducted in a typical U.S. cotton soil. See Discussion for details.

MATERIALS AND METHODS:

Thidiazuron uniformly labeled in the phenyl ring (>97% pure; specific radioactivity 11.8 MBq/mg [318.95 $\mu$Ci/mg]) was added to a German sandy loam soil (German Standard Soil 2.3) sieved to 2 mm (see Table 1 for soil properties). The soil moisture content was adjusted to approximately 78% of 0.33 bar (or 60% of its maximum water-holding capacity). $^{14}$C-Thidiazuron, which had been dissolved in methanol, was added to the soil at a rate of 0.3 mg a.i./kg which approximates the maximum field application rate of 0.2 lb a.i./A. (The dosed rate assumes uniform distribution of thidiazuron in the upper 5 cm of a soil with a bulk density of 1.5 g/cm$^3$.) $^{14}$C-Thidiazuron was applied to 22 soil samples for duplicate analysis at 11 sampling intervals (days 0, 3, 10, 30, 60, 91, 120, 150, 220, 269, and 361). Microbial biomass in soil samples was measured prior to application and on days 120, 152, and 361 in untreated and thidiazuron-treated samples.

The side arms of test flasks were filled with 10 mL of 0.1 N KOH to trap $^{14}$C-volatiles. Flasks containing test materials were incubated aerobically for 30 days in darkness at 21 ± 2°C. Twice weekly flasks were aerated and the KOH trapping solution was replaced. The $^{14}CO_2$ content of traps was measured by precipitation with $BaCl_2$. After centrifugation to remove $Ba^{14}CO_3$, residual radioactivity in trapping solutions was measured by LSC. The limit of determination for volatiles was 0.010% of the applied radioactivity.

Soil samples were extracted sequentially as follows (samples were centrifuged to separate supernatant and solids between extracts): (1) 40 mL distilled water at room temperature for 15 min; (2) 60 ± 20 mL acetonitrile (3X) in an ice bath; and (3) Soxhlet extraction of the residual soil with approx 240 mL methanol for 16 hr. Extracts were analyzed by LSC, radio-TLC, and radio-HPLC. The limits of determination for LSC for the three extracts were 0.026%, 0.005%, and 0.021%, respectively. Residual soil samples were air-dried, ground, and combusted. To analyze for bound residues, aliquots of soil from the 120 day samples were treated with 50 mL 0.1 M NaOH at 21°C for 24 hr. After centrifugation, residual soil was dried and combusted. The NaOH extract was acidified with HCl to pH 1. The humic acid fraction was allowed to precipitate at 4°C for 12 hr. After centrifugation, the pellet was redissolved in 1 N NaOH and the solids were precipitated at pH 1 as above. The pellet (humic acid fraction) was dissolved in 1 N NaOH, diluted with water, and analyzed by LSC. The supernatants were pooled, extracted with organic solvents (N-hexane, dichloromethane, and butanol), and analyzed by TLC. All fractions were analyzed by LSC.

In a parallel experiment to determine total bound residues, thidiazuron was applied to soil at a rate of 50 ppm and extracted at day 297 as described above. Samples underwent exhaustive extraction in two groups as follows: Group A - 75 g of dry, ground soil was sequentially subjected to Soxhlet extraction for 3 hr each with n-hexane, toluene, chloroform, ethyl

acetate, acetone, butanol, and acetic acid. Group B - 75 g of dry, ground soil was extracted for 15 hr with 1 M $CaCl_2$, 0.1 M EDTA, 0.1% (w/v) sodium dodecylsulfate at room temperature, and with 5 N HCl at 80°C under reflux. All extracts in both groups were analyzed by LSC.

Radio-TLC analysis was carried out using three solvent systems: (1) toluene/$CHCl_3$/acetone/acetic acid (5/3/2/0.4, v/v/v/v); (2) ethylacetate/methanol/diethylamine (9/1/0.5, v/v/v); and (3) ethylacetate/dimethylformamide (9/1, v/v). Each extract was analyzed in at least two of the above solvent systems (either 1 & 2 or 1 & 3) both directly and after mixing with analytical standards. Radioactive spots on plates were detected using a TLC linear analyzer and by autoradiography using X-ray film. Radioactivity was quantified by scraping the radioactive segments and analyzing by LSC. Radio-HPLC analysis of extracts was carried out directly or after mixing with analytical standards. The limit of determination for HPLC was ≤0.1% of the dosed radioactivity (extract 1) although in the worst case for substance distribution the limit was ≤0.04%. All LSC analyses were done in triplicate; HPLC was performed at least twice (i.e. one on each of the duplicate soil extracts for each sampling time).

DATA SUMMARY:

Soil extracts were analyzed in two TLC systems and one HPLC system, usually without any pretreatment of the original extracts. In some cases, concentration of extracts via rotary evaporation was required prior to analysis. Quantification was based on HPLC analyses. Compounds were identified by co-chromatography in the three separation systems; approximately 3% of the applied radioactivity was in compounds which were not identified. Earlier studies found $^{14}CO_2$ to be the only volatile compound produced, hence it was the only volatile analyzed for.

At time zero, 93.6% of the applied radioactivity was extractable and 1.6% was non-extractable. By the end of the 361-day study, bound residues had increased to 44.7% of the applied radioactivity, $^{14}CO_2$ accounted for 21.2%, and 25.6% was soil-extractable. Material balances averaged 97% and ranged from 90-103% during the study (Table 2).

Table 3 and Figures 2 and 3 show the concentrations (in percent of applied radioactivity) of parent and degradates during the study. The major component in soil extracts was parent thidiazuron. Small quantities of three degradates were detected:

- 1-phenyl-3-(1,2,5-thiadiazol-5-yl)urea (std 31) - maximum concentration of 0.8% of the applied radioactivity (0.002 ppm) at day 10;
- N-phenylurea (std 32) - maximum concentration of 0.3% of the applied (<0.001 ppm) at day 30; and
- 1-m-hydroxyphenyl-3-(1,2,3-thiadiazol-5-yl)urea (std 33) - maximum concentration of 0.8% of the applied (0.002 ppm) at day 30.

One unidentified polar compound (U1) was present at a maximum of 1.6% of the applied (0.005 ppm) at day 30; its concentration declined to 0.5% of the applied (<0.002 ppm) by day 361. Other polar TLC-immobile compounds comprised ≤1.3% of the applied (0.004 ppm) during the study. The half-life of parent thidiazuron was calculated to be 111 days.

At day 269, 49.4% of the radioactivity was unextractable from soil. Further extraction with NaOH found that 19% of the total radioactivity was about evenly divided between the fulvic (8.9%) and humic acid (10.4%) fractions. Further extraction of the fulvic acid fraction with butanol found that more than half of the $^{14}C$ in this phase (5.8%) was parent thidiazuron. Additional exhaustive extraction failed to remove more than 0.1% of the total bound radioactivity.

DISCUSSION:

1. The study provided data only on phenyl-labeled thidiazuron. The fate of the thiadiazol moiety (and degradates which contain this moiety and not the phenyl group) in aerobic soil conditions cannot be assessed from the study. The evolution of $^{14}CO_2$ (21.2% of the applied radioactivity was present as $^{14}CO_2$ at day 361 - Figure 4) indicates that the phenyl ring was degrading, but only small quantities of degradates similar in structure to the parent compound (1-phenyl-3-[1,2,5-thiadiazol-5-yl]urea and 1-m-hydroxyphenyl-3-[1,2,3-thiadiazol-5-yl]urea) were detected. It appears, then, that thiadiazol-containing degradates were being formed, but their presence was not detected. EFGWB believes that data for thiadiazol-labeled thidiazuron are needed to adequately understand the compound's aerobic soil metabolism. Also, a degradation pathway based on the studies' results should be proposed which shows the structures of parent and metabolites.

2. The compound 1-phenyl-3-(1,2,5-thiadiazol-5-yl)urea was present at time zero at 0.8% of the applied (which also was the maximum concentration of any identified degradation product) and occurred at this concentration again at day 10. This compound may have been present as an impurity in the initial test substance.

3. The study indicates that soil was extracted and analyzed in duplicate at each sampling day (p. 18). EFGWB therefore assumes that neither soils nor extracts were stored prior to analysis, hence storage stability data are not required.

4. The study reports that positive identification of degradates by a method beyond co-chromatography was not possible because of the low concentrations detected in soil extracts.

5. Data were presented only as percentages of the applied radioactivity in soil samples (Table 3). Residue values can be calculated by multiplying the percentage of applied radioactivity by the application rate (0.3 ppm). In addition to percentage data, actual residue values should be reported in tabular form.

6. Table 1 indicates that the texture of the German soil used was a sandy loam according to the USDA classification system, but this could not be confirmed because the particle size distribution shown is not equivalent to the USDA scale. The silt fraction in the USDA system (0.002-0.05 mm) overlaps with the sand fraction in the European system (>0.020mm).

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Pages 56 through 72 are not included.

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____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

X FIFRA registration data.

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DATA EVALUATION RECORD

STUDY 5

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CHEM 120301 Thidiazuron §162-2

FORMULATION--00--ACTIVE INGREDIENT

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STUDY ID 41945201
Feyerabend, M. 1991. Anaerobic degradation of [UL-14C]-phenyl-thidiazuron in a sandy loam soil at 21°C. Unpublished study performed by Schering AG, Berlin, Federal Republic of Germany, and submitted by NOR-AM Chemical Co. Laboratory Project ID UPSR 20/91.

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REVIEWED BY:

Arnet W. Jones, Agronomist
Review Section 1
OPP/EFED/EFGWB

Signature: Arnet W. Jones

Date: 26 APR 1993

APPROVED BY:

Paul J. Mastradone, Ph.D.
Chief, Review Section 1
OPP/EFED/EFGWB

Signature: Paul J. Mastradone

Date: 26 APR 1993

CONCLUSIONS:

Metabolism - Anaerobic Soil

1. The study is acceptable and fulfills the anaerobic soil metabolism data requirement (162-2) for thidiazuron.

2. Following 30 days of aerobic incubation, thidiazuron (nominal concentration 0.3 ppm) was incubated anaerobically in a German sandy loam soil in darkness at 21°C for 90 days. During the anaerobic phase, thidiazuron degraded with a half-life of >90 days (the extrapolated half-life was 410 days). At day 37 (7 days after initiation of anaerobic conditions), the degradate N-m-hydroxyphenyl-N'-(1,2,3-thiadiazol-5-yl)urea comprised 0.9% of the applied (0.003 ppm), which was the highest concentration of any identified degradate during the anaerobic incubation period. One unidentified polar degradate (compound U1) comprised 1.6% (0.005 ppm) and 1.4% of the applied (0.004 ppm) at days 30 and 37, respectively. By the end of the study, 31.6% of the applied radioactivity was present in bound residues and $^{14}CO_2$ accounted for 1.8%, virtually all of which had evolved during the aerobic phase.

3. No additional anaerobic soil metabolism data are required for thidiazuron at this time.

MATERIALS AND METHODS:

Thidiazuron uniformly labeled in the phenyl ring (>97% pure; specific radioactivity 11.8 MBq/mg [318.95 $\mu$Ci/mg]) was added to a German sandy loam soil (German Standard Soil 2.3) sieved to 2 mm (see Table 1 for soil properties). The soil moisture content was adjusted to approximately 75% of 0.33 bar (or 58% of its maximum water-holding capacity). $^{14}$C-Thidiazuron, which had been dissolved in methanol, was added to the soil at a rate of 0.3 mg a.i./kg which approximates the maximum field application rate of 0.2 lb a.i./A. (The dosed rate assumes uniform distribution of thidiazuron in the upper 5 cm of a soil with a bulk density of 1.5 g/cm$^3$.) $^{14}$C-Thidiazuron was applied to 18 soil samples for duplicate analysis at nine sampling intervals (days 0, 3, 10, and 30 - aerobic conditions; and days 37, 44, 60, 91, and 120 - anaerobic conditions). Microbial biomass in soil samples was measured prior to application and on day 120 in aerobic conditions (untreated and thidiazuron-treated samples).

The side arms of test flasks were filled with 10 mL of 0.1 N KOH to trap $^{14}$C-volatiles. Flasks containing test materials were incubated aerobically for 30 days in darkness at 21 ± 2°C. Twice weekly during the aerobic phase flasks were aerated and the KOH trapping solution was replaced. After 30 days, the remaining 10 flasks were waterlogged with approx 40 mL $N_2$-flushed, deionized water and then flushed with $N_2$ for approx 30 min. Trapping solutions were replaced with fresh $N_2$-flushed solution and flasks were sealed with hot paraffin. Volatiles traps were analyzed weekly by LSC. The $^{14}CO_2$ content of traps was measured by precipitation with $BaCl_2$. After centrifugation to remove $Ba^{14}CO_3$, residual radioactivity in trapping solutions was measured by LSC. The limit of determination for volatiles was 0.010% of the applied radioactivity.

Soil samples were extracted and analyzed in duplicate on day 0 (day of treatment), days 3, 10 (aerobic incubation), day 30 (day of flooding) and on days 37, 44, 60, 91, and 120 (anaerobic incubation period). Samples were extracted sequentially as follows (samples were centrifuged to separate supernatant and solids between extracts): (1) 40 mL distilled water at room temperature for 15 min (aerobic samples only); (2) 60 ± 20 mL acetonitrile (3X) in an ice bath; and (3) Soxhlet extraction of the residual soil with approx 240 mL methanol for 16 hr. Extracts were analyzed by LSC, radio-TLC, and radio-HPLC. The limits of determination for LSC for the three extracts were 0.026%, 0.005%, and 0.021%, respectively. Residual soil samples were air-dried, ground, and combusted. To analyze for bound residues, aliquots of soil from the 120 day samples were treated with 50 mL 0.1 M NaOH at 21°C for 24 hr. After centrifugation, residual soil was dried and combusted. The NaOH extract was acidified with HCl to pH 1. The humic acid fraction was allowed to precipitate at 4°C for 12 hr. After centrifugation, the pellet was redissolved in 1N NaOH and the solids were precipitated at pH 1 as above. The pellet (humic acid fraction) was dissolved in 1N NaOH, diluted with water, and analyzed by LSC. The supernatants were pooled, extracted with organic solvents (N-

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hexane, dichloromethane, and butanol), and analyzed by TLC. All fractions were analyzed by LSC.

Radio-TLC analysis was carried out using three solvent systems: (1) toluene/$CHCl_3$/acetone/acetic acid (5/3/2/0.4, v/v/v/v); (2) ethylacetate/methanol/diethylamine (9/1/0.5, v/v/v); and (3) ethylacetate/dimethylformamide (9/1, v/v). Each extract was analyzed in at least two of the above solvent systems (either 1 & 2 or 1 & 3) both directly and after mixing with analytical standards. Radioactive spots on plates were detected using a TLC linear analyzer and by autoradiography using X-ray film. Radioactivity was quantified by scraping the radioactive segments and analyzing by LSC. Radio-HPLC analysis of extracts was carried out directly or after mixing with analytical standards. The limit of determination for HPLC was ≤0.1% of the dosed radioactivity (extract 1) although in the worst case for substance distribution the limit was ≤0.04%. All LSC analyses were done in triplicate; HPLC was performed at least twice (i.e. one on each of the duplicate soil extracts for each sampling time).

DATA SUMMARY:

At time zero, 93.6% of the applied radioactivity was extractable and 1.6% was non-extractable. By the end of the 30-day aerobic incubation period, bound residues had increased to 18.9% of the applied radioactivity and $^{14}CO_2$ accounted for 1.8%. At the end of the anaerobic phase (day 120), 69.4% of the applied radioactivity was extractable, no further $^{14}CO_2$ had evolved, and bound residues had increased to 31.6% of the applied.

The major component in all extracts throughout the study was parent thidiazuron. It comprised 92.2% of the applied at day 0 and 74.7% at day 30 (the end of the aerobic phase). At the end of the anaerobic period (day 120), parent accounted for 67.4% of the applied radioactivity (Table 3).

Table 3 shows the distribution of parent thidiazuron and its metabolites identified by HPLC co-chromatography with standards. The degradate N-phenyl-N'-(1,2,5-thiadiazol-5-yl) urea (std. 31) comprised 0.8% of the applied (0.002 ppm) at day 10 which was the highest concentration of any degradate during the aerobic phase (Table 3). At day 37 (7 days after initiation of anaerobic conditions) N-m-hydroxyphenyl-N'-(1,2,3-thiadiazol-5-yl)urea (std. 33) comprised 0.9% of the applied (0.003 ppm), which was the highest concentration of any identified degradate during the anaerobic incubation period. One unidentified polar compound (U1) comprised 1.6% (0.005 ppm) and 1.4% of the applied (0.004 ppm) at days 30 and 37, respectively (Table 3). The concentration of this compound declined to 0.4% of the applied (0.001 ppm) by day 120.

At the end of the study, soil-bound material (defined as residues not extractable from the initial extraction processes) comprised 31.6% of the applied radioactivity. Further extraction of this material with 0.1N NaOH removed about one-third of this (11.6% of the total). An average of 7.6% of the applied was found in the fulvic acid fraction with about 4.4% co-precipitating with the humic acid fraction. Following extraction of the



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fulvic acid supernatant with dichloromethane and butanol, TLC analysis indicated that >60% of the residues were present as parent. Further extraction with aqueous salt, chelator, and detergent solutions removed about 0.3% of the applied radioactivity. Also, extraction with weak (acetic) and strong (5 N HCl) acid removed about 5% of the applied radioactivity, but characterization of this material was not possible.

The calculated half-life for thidiazuron for the anaerobic phase (days 30-120) was 410 days. The overall half-life (30 days aerobic + 90 days anaerobic incubation) was reported to be 201 days. Material balances were 93-103% throughout the study (Table 2).

DISCUSSION:

1. The study indicates that soil was extracted and analyzed in duplicate at each sampling day (p. 19). EFGWB therefore assumes that neither soils nor extracts were stored prior to analysis, hence storage stability data are not required.

2. Table 3 reports the application rate as 2.2 ppm. The actual application rate (upper 5 cm of soil) based on information provided in the study narrative was 0.3 ppm. The concentrations reported in the Data Summary are based on an initial soil application rate of 0.3 ppm.

3. The study reports that positive identification of degradates was not possible because of the low concentrations detected in soil extracts.

4. Redox values, which could have confirmed anaerobic conditions, were not reported. EFGWB prefers that anaerobicity be confirmed by measuring and reporting Eh at each sampling interval. It appears, however, that anaerobic conditions were maintained because of the difference in degradation rates and $^{14}CO_2$ evolution between the aerobic and anaerobic phases and because the experimental design appeared to ensure anaerobicity.

5. Data were presented as percentages of the applied radioactivity present in soil samples; actual residue values were not presented. EFGWB prefers that actual residue values be reported in addition to the percentages of applied radioactivity.

6. It is difficult to confirm the $^{14}CO_2$ concentrations reported in the study narrative with the data shown in Table 4. The graphic presentation (Figure 4) outlines $^{14}CO_2$ evolution more clearly.

7. Table 1 indicates that the texture of the German soil used was a sandy loam according to the USDA classification system, but this could not be confirmed because the particle size distribution shown is not equivalent to the USDA scale. The silt fraction in the USDA system (0.002-0.05 mm) overlaps with the sand fraction in the European system (>0.020mm).



94 93

DATA EVALUATION RECORD

STUDY 6

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CHEM 120301 Thidiazuron §163-1

FORMULATION--00--ACTIVE INGREDIENT

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STUDY ID 41364909
Bruhl, R. 1988. W61 thidiazuron: Adsorption to and desorption from soil. Study No. PF-S 87 057. Report No. UPSR 17/88 - PA 49 537.7/6. Unpublished study performed by Schering AG, Berlin, Germany, and submitted by Nor-Am Chemical Company, Wilmington, DE.

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DIRECT REVIEW TIME = 4

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28 APR 1993

CONCLUSIONS:Z

Mobility - Leaching and Adsorption/Desorption

1. This study is acceptable and partially fulfills the leaching and adsorption/desorption data requirement (163-1) by providing information on the mobility (batch equilibrium) of unaged thidiazuron in foreign soils classified as sand, loamy sand, sandy loam, and sandy clay loam.

2. Thiadiazol-labeled thidiazuron was slightly mobile to relatively immobile in non-U.S. soils classified as sand, loamy sand, sandy loam, and sandy clay loam soils. Respective Freundlich $K_{ads}$ values for these soils were 4.36, 16.2, 7.33, and 18.78. Adsorption increased with increasing soil organic carbon content and CEC. See Discussion for details.

3. No additional information on the mobility of unaged thidiazuron in soil is needed at this time. Information is needed on the mobility of phenyl- and thiadiazol-labeled [$^{14}$C]thidiazuron residues aged aerobically for 30 days or one half-life (whichever is shorter) prior to leaching. The aged

residues study should be conducted in typical U.S. cotton-growing soils which contain <1% organic matter.

METHODOLOGY:

Sand, loamy sand, sandy loam, and sandy clay loam soils (Table 1) were air-dried and sieved (2 mm). Based on preliminary experiments to define test parameters, an equilibration time of 24 hours was selected for the soils. It was also determined that adsorption of the test substance to glass surfaces was insignificant (1-3%); the length of the equilibration period was not specified.

For the adsorption studies, 20 g samples of soil were transferred to centrifuge tubes and equilibrated with 0.01 M calcium chloride solution (volume unspecified) for 12-16 hours at 25°C. Following the equilibration period, the soil:solution slurries were centrifuged; the supernatant was removed and replaced with 0.6-77.5 mL of a 0.01 M calcium chloride solution containing approximately 6.9 µg/mL of thiadiazol-labeled [5-$^{14}$C]thidiazuron (radiochemical purity >93%, specific activity 67.57 mCi/g, Schering AG). Additional calcium chloride solution was added to bring the final solution volume to approximately 100 mL; final concentrations of [$^{14}$C]thidiazuron were determined to be 0.0393-0.0435, 0.200-0.207, 0.992-1.01, and 4.87-5.04 µg/g solution (Tables 3.1-3.4). The soil:solutions slurries were shaken at 25°C for approximately 26 hours. After the shaking period, the slurries were centrifuged. A 30-mL aliquot of each supernatant was removed; aliquots (0.5 mL) were analyzed for total radioactivity using LSC. Additional aliquots of the supernatants containing the highest concentration of [$^{14}$C]thidiazuron were analyzed using TLC on silica gel plates developed in acetone:diethylether (1:1, v:v) and ethyl acetate:dimethylformamide (9:1, v:v). Radioactive areas were detected and quantified using a TLC linear analyzer; radioactive compounds were also detected using autoradiography.

Desorption of thidiazuron was determined by replacing the 30 mL of supernatant removed after adsorption with an equal volume of pesticide-free 0.01 M $CaCl_2$ solution. The soil:solution slurries were shaken at 25°C for 1.5 hours. After shaking, the slurries were centrifuged and a 40-mL aliquot of each supernatant was analyzed by LSC. The 40-mL of supernatant was replaced and the desorption procedure was repeated two more times by removing a 50-mL aliquot of supernatant each time. Following the desorption experiment, the soils were extracted twice with methanol or acetone; aliquots (0.5 mL) of the extracts were analyzed by LSC and TLC as described above. The extracted soils were analyzed for total radioactivity by LSC following combustion.

DATA SUMMARY:

Based on batch equilibrium studies, thiadiazol-labeled [5-$^{14}$C]thidiazuron (radiochemical purity >93%), at approximately 0.04, 0.2, 1.0, and 5.0 µg/g solution, was determined to be slightly mobile to relatively immobile in sand, loamy sand, sandy loam, and sandy clay loam soil:calcium chloride

solution slurries (1:5, w:v) that were equilibrated for 26 hr at 25°C . Freundlich $K_{ads}$ values were 4.36 for the sand soil (German standard soil 2.1), 16.2 for the loamy sand soil (German soil 2.2), 7.33 for the sandy loam soil (German soil 2.3), and 18.78 for the sandy clay loam soil (Schering [British] soil 171); respective $K_{oc}$ values were 908, 786, 780, and 494 (Tables 4.1-4.4). Adsorption increased with increasing soil organic carbon content and CEC. $K_{des}$ values were 0.425-7.21 for the sand soil, 0.378-17.51 for the loamy sand soil, 0.342-9.996 for the sandy loam soil, and 0.432-19.31 for the sandy clay loam soil. It was reported that TLC analysis of solutions following adsorption and soil extracts following desorption indicated that thidiazuron did not degrade during the study; quantitative data were not provided. Material balances ranged from 95.4 to 99.3% of the applied radioactivity.

DISCUSSION:

1. The study indicates that thidiazuron is not likely to be mobile in U.S. cotton soils. For German soil 2.1, a sand low in organic matter with high leaching potential (67.6% of the particles are 0.2-2 mm; 0.48% organic carbon [0.83% O.M.]), the reported $K_{ads}$ was 4.4 (Tables 1 and 4.1).

2. Leaching and adsorption/desorption data are needed for aged thidiazuron residues. Because the batch equilibrium data were derived from non-U.S. cotton soils, and because thidiazuron is used exclusively on cotton, the aged leaching study should be conducted in typical U.S. cotton soils.

3. Four foreign soils (3 German & 1 British) were used in this study. No data were presented which compare them to U.S. soils. The mobility data should be based on soils typical of those on which the chemical will be used.

4. The textural classifications of the three German soils (sand, loamy sand, and sandy loam) and one United Kingdom soil (sandy clay loam) could not be compared directly with the same soil textures as defined by the USDA soil classification system because of different particle size distributions. In study soils the sand fraction (0.02-2 mm) overlaps with the silt fraction of the USDA system (0.002-0.05 mm). The particle size distribution as reported by the study author was coarse sand - 0.2-2 mm; fine sand - 0.02-0.2 mm; silt - 0.002-0.02 mm, and clay - <0.002 mm. The U.K. sandy clay loam soil had deviating particle sizes: sand 0.212-2 mm and fine sand 0.02-0.212 mm. The USDA system classifies soil particles according to the following size distributions: clay - <0.002 mm; silt - 0.002-0.05 mm; and sand - 0.05-2 mm.

5. Quantitative data from the preliminary experiments performed to determine the equilibration time and if the test substance adsorbed to glassware were not provided to review.

6. It could not be determined whether one- or two-dimensional TLC was used to analyze the supernatants and soil extracts and how the radioactive compounds were identified.

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Pages 98 through 118 are not included.

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____ The product confidential statement of formula.

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DATA EVALUATION RECORD

STUDY 7

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CHEM 120301 Thidiazuron §164-1

FORMULATION--06--WETTABLE POWDER (WP)

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STUDY ID 41761105
Wrede-Rucker, A. 1990. W67 thidiazuron: Dissipation of thidiazuron in soil following application of Dropp 50WP to bare ground - USA 1989. Study No. PF-R 89 068. Report No. UPSR 65/90 - PA 49 537.7/16. Unpublished study performed by Schering AG, Berlin, Germany, and submitted by NOR-AM Chemical Company, Wilmington, DE.

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DIRECT REVIEW TIME = 6

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28 APR 1993

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study provides supplemental information regarding the terrestrial field dissipation of thidiazuron.

2. Thidiazuron did not dissipate from the upper 8 cm (3.1 inches) of a bare ground plot of sandy loam soil in Florida in the 9 months following the second of two applications (7-day interval) of thidiazuron (Dropp 50% WP) at 0.168 kg a.i./ha (0.336 kg a.i./ha total). Thidiazuron was detected in small quantities at several sampling intervals at the 15-30 cm depth; it was not detected (<0.25 ppm) deeper than 30 cm. Small quantities of the degradates photothidiazuron [1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea and thidiazolylurea were detected during the study.

3. This study is scientifically sound, but cannot be used to fulfill the data requirement for the following reasons:

   (a) the study was conducted for only 9 months, which was insufficient to assess a pattern of decline of the test substance;

   (b) the test soil was not completely characterized;

   (c) field test data, including meteorological data, were incomplete; and

   (d) field maintenance practices were not adequately reported.

4. Because the study was terminated before either the pattern of decline of thidiazuron was established or 18 months after the final application, the problems with this study cannot be resolved by the submission of additional data. Two new field dissipation studies should be conducted at sites in the U.S. where cotton is cultivated. Also, a long-term field dissipation study may be required. See Discussion for details.

METHODOLOGY:

Thidiazuron (Dropp 50 WP, 490 g a.i./kg, source not specified) was broadcast-applied twice at 0.168 kg a.i./ha at a 7-day interval to a bare ground plot (24 x 48 m) of sandy loam soil (2.12% organic matter, pH 6.3) located in Molino, Florida, on September 5 and 12, 1989. The treated plot was rototilled (depth unspecified) at 2 and 8 days after the second application. An untreated plot (12 x 48 m) was maintained as a control; a 72-m buffer zone separated the treated and untreated plots. Three soil cores (diameter unspecified, 0- to 81-cm depth) were collected from the treated plot prior to the first application, immediately after each application, and at 1, 7, 17, 28, 62, 122, 182, and 273 days after the second application. The untreated plot was sampled prior to the first application and at 1, 28, and 182 days after the second application. Cores were divided into 0- to 8-, 8- to 15-, 15- to 30-, 30- to 46-, 46- to 61-, 61 to 76-, and 76- to 81-cm segments; the soil samples were stored frozen at -20 C for approximately 2-14 months prior to analysis.

Soil samples were Soxhlet-extracted for 6-7 hours with methanol. The extract was evaporated to dryness; the resulting residue was redissolved in ethyl acetate and passed through a C-18 Sep-Pak cartridge. The Sep-Pak was washed with additional ethyl acetate. Eluates were collected, evaporated to dryness, redissolved in methanol, and analyzed for thidiazuron, its isomer photothidiazuron [1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea], and the degradates thidiazolylurea and phenylurea. Analyses were conducted using HPLC with UV (235 or 280 nm) detection and a mobile phase of water:methanol (ratio dependent on the compound). Detection limits were 0.01 ppm for thidiazuron, thidiazolylurea, and phenylurea and 0.02 ppm for photothidiazuron; the limit of determination was 0.025 ppm for all four compounds. Recovery efficiencies from soil samples fortified with thidiazuron at 0.025-0.1 ppm ranged from 56.3 to 116.3% (mean 81%) of the applied, 1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea at 0.025-0.1 ppm ranged

from 61.0 to 121.6% (mean 94%), thidiazolylurea at 0.025-0.1 ppm ranged from 65.2 to 118.3% (mean 86%), and phenylurea at 0.025-0.05 ppm ranged from 68.8 to 99.6% (mean 88%). Results were expressed on a dry soil basis and corrected for recovery efficiency.

DATA SUMMARY:

Thidiazuron did not dissipate from the upper 8 cm (3.1 inches) of a bare ground plot (24 x 48 m) of sandy loam soil in Florida during the 9 months following the second of two applications (7-day interval) of thidiazuron (Dropp 50% WP) at 0.168 kg a.i./ha (0.336 kg a.i./ha total) in September of 1989. In the 0- to 8-cm soil layer, thidiazuron (ZK 49 537) ranged from an average 0.11 to 0.23 ppm (maximum 0.356 ppm at 1 day after second treatment) during the 9-month study (Table 3.1 and Appendix V). Thidiazuron was detected in the 8- to 15-cm soil depth once, at 0.026 ppm at 122 days after the second treatment, and in the 15- to 30- cm soil depth six times, at 0.025 and 0.027 ppm immediately after the first treatment, at 0.074 and 0.037 ppm at 1 day after the second treatment, at 0.028 ppm at 28 days after the second treatment, and at 0.046 ppm at 122 days after the second treatment (Appendix V). Thidiazuron was not detected (<0.025 ppm) in the 30-to 46-, 46- to 61-, 61- to 76-, and 76- to 91-cm soil depths. The isomer

photothidiazuron [1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea; ZK 80 178]

was detected twice in the 0- to 8-cm soil depth, at 0.040 ppm at 1 day after the second treatment and 0.041 ppm at 28 days after the second treatment. It was detected twice in the 8- to 15-cm depth, at 0.047 ppm at 1 day after the second treatment and 0.034 ppm at 17 days after the second treatment, and once in the 15- to 30-cm depth, at 0.070 ppm at 273 days after the second treatment. Photothidiazuron was not detected in soil depths below 30 cm. The degradate

thidiazolylurea (ZK 85 290)

was only detected once, at 0.027 ppm in the 8- to 15-cm soil depth at 273 days after the second treatment, and was <0.025 ppm at all other sampling intervals and soil depths. The degradate

phenylurea (ZK 44 483)

was <0.025 ppm in all soil samples analyzed.

During the initial 6 months of the study (9/5/89-3/13/90), rainfall plus irrigation totaled 44.3 inches (1125.06 mm); air and soil temperatures were not reported.

DISCUSSION:

1. The study was conducted for an insufficient length of time to achieve one of its main objectives, i.e. to assess the pattern of decline of the parent compound and the patterns of formation and decline of major degradates under typical field use conditions. Since the compound is stable, terrestrial field dissipation studies on thidiazuron should be conducted until this objective is achieved, or for 18 months after the final application. Also, acceptable data are needed from a minimum of two typical use sites, hence both sites should be typical of U.S. cotton production unless other uses are intended (see Subdivision N guidelines).

2. The soil at the Florida site contained 2.12% organic matter which is not typical of cotton soils. Most U.S. cotton is grown in relatively warm soils which are not rich in organic matter. Of the top 19 soil series suited to cotton cultivation, organic matter content ranges from 0.3 to 2.0%. Seventeen of these 19 soils have ≤1.3% organic matter.[1] Because thidiazuron is used exclusively on cotton and because its mobility is related to soil organic matter, two field dissipation studies should be carried out on typical U.S. cotton soils which are low in organic matter. The studies should be carried out in two distinct locations where thidiazuron is typically used and should include application of thidiazuron to bare ground at the maximum application rate.

3. Several data requirements, including aerobic soil metabolism (162-1), have not been fulfilled. Terrestrial field dissipation studies should address the concentration and fate of parent and significant degradates from soil metabolism and other laboratory studies, hence acceptable laboratory data should be submitted prior to beginning field studies.

4. Freezer storage stability data were not submitted; however, the data indicate that thidiazuron was stable during storage for this study. Specific lengths of storage time for the soil samples could not be determined from the information provided; it appears that samples were stored frozen from 2 to 14 months prior to analysis. If any isomerization or degradation of thidiazuron were to occur during a complete 18-month terrestrial field dissipation study, storage stability data should be submitted.

5. The test soil was not completely characterized; the textural analysis (percent sand, silt, and clay) and CEC value were not provided.

6. Field test data were incomplete. The depth to the water table and slope of the field were not reported. Air and soil temperatures for the study period were not provided, and total precipitation was only reported for the initial 6 months of the 9-month study.

7. Preparation of the plot prior to treatment was not described.

8. Except for reporting that the treated plot was irrigated and rototilled at 2 and 8 days after the second application, field maintenance procedures were not reported.

9. The results from this study indicate that thidiazuron did not dissipate or degrade during 9 months after two applications to bare ground sandy loam soil; however, in a soil photolysis study (Study 2, MRID 41364902), thiadiazol-labeled [5-$^{14}$C]thidiazuron, isomerized rapidly (observed half-life <0.5 hours) on sandy loam soil that was continuously irradiated with a xenon arc lamp; the photoproduct formed was the isomer 1-phenyl-3-(1,2,5-thiadiazol-3-yl)urea. It is recognized that differences in rates of dissipation or degradation often occur between field and laboratory studies, and it was not obvious what variable(s) may have resulted in the stability of thidiazuron in the field.

10. The study author reported that the concentrations of thidiazuron detected in 0-8 cm soil layer were approximately 50% of the concentration expected from the application rate. The target application rate was 336 g a.i./ha (two applications at 0.168 kg a.i./ha) which is equivalent to approximately 0.3 lb a.i./A. A target application rate of 0.3 lb a.i./A would be expected to result in approximately 0.3 ppm in the 0-3 inch soil layer. At time zero after the second application, the average concentration in the 0-3.1 inch (0-8 cm) soil layer was 0.14 ppm, or slightly less than 50% of expected. One day after the second application, the average concentration of thidiazuron was 0.23 ppm, or about 78% of the target rate.

11. A long-term field dissipation study may be needed to assess the dissipation of thidiazuron under field use conditions. Long-term terrestrial field dissipation studies typically are needed if >50% of the test substance remains undegraded at the time of the next recommended application.

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[1] Griggs, R.H., et al. 1991. Documentation and User's Manual for Pesticide Registration and Environmental Assessment Program (PRE-AP). Version 1.2. Texas Agricultural Experiment Station, Temple, TX.

Page_____ is not included in this copy.

Pages 124 through 149 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

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____ The product confidential statement of formula.

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DATA EVALUATION RECORD

STUDY 8

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CHEM 120301 Thidiazuron §165-1

FORMULATION--00--ACTIVE INGREDIENT

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STUDY ID 00030793
Bruhl, R. 1978. Rotational plant uptake study with radioactive SN 49 537. Unpublished study performed by Schering AG and submitted by NOR-AM Chem. Co.

STUDY ID 41364907
Bruhl, R. 1979. W47 Appendix: Rotational plant uptake study with radioactive SN 49 537. Unpublished study performed by Schering AG and submitted by NOR-AM Chem. Co.

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REVIEWED BY:

Arnet W. Jones, Agronomist
Review Section 1
OPP/EFED/EFGWB

Signature: Arnet W. Jones.
Date: 28 APR 1993

APPROVED BY:

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OPP/EFED/EFGWB

Signature: Paul J. Mastradone
Date: 28 APR 1993

CONCLUSIONS:

Accumulation - Confined Rotational Crops (165-1)

1. The study provides supplemental information regarding the uptake of thidiazuron by confined rotational crops.

2. Soybeans, sugarbeets, and sorghum were planted in soil which had been treated 2 weeks (first growing period) or 6 months (second growing period) earlier with phenyl or thiadiazol-labeled thidiazuron (0.2 ppm). For soybeans (first growing period) the reported residue levels (in parent equivalents) for both radiolabeled groups were the following: leaves and stems - <0.01-0.06 ppm; fruit - <0.01-0.16 ppm; and roots - <0.01-0.15 ppm. Residues for the second growing period were ≤0.07 ppm for all plant parts. In sugarbeets residue levels were ≤0.07 ppm and ≤0.01 ppm for the first and second growing periods, respectively for both labeled groups. Total residues in sorghum leaves, stems, and fruit (first growing period) were ≤0.01 ppm for each harvest interval. In roots, total residues were 0.01-0.09 ppm. For the second growing period, residues in sorghum (thidiazol-labeled treatment) were 0.01-0.03 ppm in mature leaves and stems. In mature sorghum fruit and roots, respective residue levels were 0.05-0.13 ppm and ≤0.01-0.03 ppm for both labeled treatments.

3. The study cannot be used to fulfill data requirements for the following reasons:

a) The study soil contained approximately 3.4% organic matter. This relatively high organic matter content is not typical of U.S. cotton soils which normally contain <1% organic matter. The study soil may have bound thidiazuron and limited its availability to rotational crops in a manner which would not be observed in actual field use. See Discussion.

b) Insufficient data were presented concerning the conditions under which the study was conducted. See Discussion.

c) There was no apparent confirmation of the pesticide application rate to the test soil.

d) Residues in plants were not characterized adequately.

e) The length of storage time and storage conditions for plant and soil samples were not reported. Frozen storage stability data were not presented.

4. It appears that new data are required. Because thidiazuron is used exclusively as a cotton defoliant, the new study should be conducted in U.S soils typical of cotton production and should incorporate rotational intervals and crops associated with cotton cultivation.

MATERIALS AND METHODS:

A dry German loamy sand soil (88.2% sand; 5.5% silt; 6.35% clay; 2.0% organic carbon; pH 6.6; CEC 7.5 mVal/100g; see discussion) was fortified to 0.2 ppm with $^{14}$C-phenyl-labeled or 5-$^{14}$C 1,2,3-thidiazol-thidiazuron, placed in 10L buckets, and moistened. Soybeans, sorghum, or sugarbeets were planted in the soil after aging periods of 14 days (first growing period) and 6 months (second growing period). Control plants were grown in untreated soil and analyzed at the same time intervals as plants in treated pots. Plants were divided into three parts (leaves and stems, roots, and fruiting parts) which were analyzed at ¼ maturity (first harvest), ½ maturity (second harvest), and full maturity (third harvest).

For the first growing period, first and second harvests, plant parts were homogenized and extracted with methanol. Extracts were analyzed for total radioactivity by LSC. All other analyses, including part of the ½ maturity harvest, first growing period, were carried out by freeze-drying, combustion, and LSC. Plant material was not extracted because low residue concentrations were anticipated.

Soil samples were assayed for total radioactivity immediately after treatment, at planting time, and at the same intervals as plants. About 50 g of soil was extracted three times with dioxane or toluene. This was followed by an extraction with 50 mL of methanol and a 2.5 hr Soxhlet extraction with 300 mL of methanol. Soil extracts were analyzed by LSC.

20 g of the extracted soil was then shaken with 25 mL of 0.5N NaOH for 24 hr and the dissolved material was separated into fulvic and humic acids. Extracted soil was combusted and counted by LSC to quantify non-extractable radioactivity.

In an attempt to characterize $^{14}C$ residues in sorghum and soybean grain from the third harvest, second growing period (see the 11/14/78 review of MRID no. 00030793), fruits were ground and extracted with methanol. Extracts were filtered and the tissue was washed with methanol. Extract samples were assayed for $^{14}C$ by LSC. Tissue samples were combusted and analyzed for $^{14}C$.

Appendix to the Original Study (MRID no.41364907)

In an attempt to characterize $^{14}C$ residues in sorghum and soybean grain from the third harvest, second growing period (see the 11/14/78 review of MRID no. 00030793), fruits were ground and extracted with methanol. Extracts were filtered and tissue washed with methanol. Extract samples were assayed for $^{14}C$ by LSC. Tissue samples were combusted and analyzed for $^{14}C$.

REPORTED RESULTS:

Tables 1 through 3 and 7 through 9 summarize crop fresh weights at harvest, the number of plants per batch, and the numbers of "fruit". Soybeans (fruit) and sugarbeets were very small at maturity. Tables 4 through 6 and 10 through 12 summarize residue concentrations. The report states that "Because of the low residues found in all plant parts, chromatographic analysis was impossible." All residue concentrations are reported as thidiazuron equivalents on a plant fresh weight basis and are corrected for values found in control plants.

Table 4 shows residue concentrations in soybeans grown in soil which had been treated with 0.2 ppm thidiazuron 2 weeks prior to planting. At the first growing period, residues in leaves and stems ranged from <0.01 to 0.06 ppm. In fruit, residue concentrations ranged from <0.01 to 0.04 ppm for phenyl-labeled thidiazuron. For thidiazol-labeled thidiazuron, fruit residues ranged from <0.01 ppm (second harvest - 12 weeks after planting) to 0.16 ppm (first harvest - 6 weeks after planting).

At the second growing period (0.2 ppm thidiazuron was aged in soil for 6 months prior to planting - Table 10), residue concentrations were lower than for the first growing period. In leaves and stems, residues >0.01 ppm were observed only in plants harvested at maturity. In fruit, residues were detected only in plants harvested at maturity (third harvest), with residue concentrations ranging from 0.03 to 0.07 ppm. In soybean roots, residue concentrations ranged from 0.01 to 0.04 ppm. Residues in roots were stated to be "of no importance and have to be accepted with caution." Their presence "might be due to direct contact with radioactive soil" and "insufficient rinsing with water."

Table 5 shows residue concentrations in sugarbeets grown in soil which had been treated with 0.2 ppm thidiazuron 2 weeks prior to planting. In aerial parts, residues of 0.02 and 0.01 ppm were detected only at the first harvest (6 weeks after planting) for phenyl- and thidiazol-labeled thidiazuron, respectively. There were no other detections in aerial parts in the 2-week rotational sugarbeets. In beets, residue levels were 0.03-0.07 ppm for the first harvest. A residue level of 0.03 ppm was detected in one batch of beets at the second harvest period.

In sugarbeets grown in soil treated 6 months earlier with radiolabeled thidiazuron (Table 11), a residue level of 0.01 ppm was detected in the aerial parts of one batch of plants treated with thidiazol-labeled thidiazuron harvested at maturity. There were no other detections in sugarbeets grown in soil treated 6 months earlier with thidiazuron.

Table 6 shows residue concentrations in sorghum grown in soil which had been treated with 0.2 ppm thidiazuron 2 weeks prior to planting. Total residues in leaves and stems and fruit were $\leq$0.01 ppm for each harvest interval. In roots, total residues expressed as thidiazuron equivalents ranged from 0.01 to 0.09 ppm. Root residues were attributed to "contaminations by the radioactive soil."

Table 12 shows residue concentrations in sorghum grown in soil which had been treated with 0.2 ppm thidiazuron 6 months prior to planting. Residue concentrations in the thidiazol-labeled treated plants ranged from 0.01-0.03 ppm in leaves and stems harvested at maturity. There were no other detections of radioactivity in leaves and stems. In mature fruit (third harvest), residues of 0.05-0.09 ppm were detected in plants grown in thidiazol-labeled treated soil. In sorghum fruit grown in phenyl-labeled treated soil at the same harvest period, residues were 0.09-0.13 ppm. In roots, residue levels ranged from $\leq$0.01-0.03 ppm for both labeled treatments and across harvest periods. There were no fruit available for analysis from the first harvest period (6 weeks after planting).

Tables 13-18 show soil residue concentrations for the two radiolabeled compounds used for each crop and each harvest interval. Extractable residues ranged from 1-40% of the total radioactivity recovered. Much of the balance of residues were bound to the organic or mineral fractions of the soil. The study reports that "radioactivity decreased to about 0.10 ppm" during the experiment. It also reports that "thin-layer chromatograms from early extractions showed a metabolite pattern not significantly different from that already observed in soil degradation studies."

Appendix to Original Study (MRID no. 41364907)

No detectable (<0.01 ppm) radioactivity was found in extracts. All radioactivity (0.05-0.09 ppm) was detected by combustion of plant material. The study author stated that "the $^{14}C$ measured seemed to be incorporated into the plant matrix" and that "low amounts of radioactivity detected in plant parts at maturity could not be explained with the uptake of intact SN 49 537 (thidiazuron) from the soil."

DISCUSSION:

1. The German soil used in this study contained 2.0% organic carbon, which translates to approximately 3.4% organic matter (as a general rule, % organic matter = % organic carbon X 1.724). This soil is not representative of U.S. cotton soils which typically contain <1% organic matter. In this lab study, the soil organic matter may have bound thidiazuron, thereby reducing its availability for rotational crop uptake. (Thidiazuron's adsorption behavior is related to soil organic matter content - see DER for Study 6). In actual field use, a greater quantity of thidiazuron could be available for rotational crop uptake because of less binding to organic matter. Rotational crop uptake studies should be conducted with typical cotton soils since thidiazuron is used exclusively as a cotton defoliant.

2. There was insufficient information provided pertaining to crop varieties, stage of plant growth at sampling, and the conditions under which plants were grown (water, light, temperature, fertilizer, indoor vs. outdoor, the number of plants per container, etc.). For example, it is not clear whether soybean "fruit" referred to seeds alone or seeds plus pods. Nor was is it clear how residue concentrations in soybean "fruit" could be measured only 6 weeks after planting. In many cases, soybeans do not flower until 6 weeks or more after planting (although this depends upon maturity group, variety, and planting date); pod and seed development occurs after flowering. Neither soybean variety nor stage of plant development at sampling was specified.

3. There is evidence that growing conditions were not optimal, or that growing conditions were not constant for the two groups of crops treated with the radiolabel in different positions. For example:

   a) Table 1 indicates that the mass of "fruit" at the first harvest (6 weeks after planting) varied widely between the phenyl- and thidiazol-labeled batches. In the phenyl-labeled group, fruit weighed 10.6 and 7.2 g for the two batches; in the two thidiazol-labeled batches, fruit weighed 2.3 and 2.6 g.

   b) Leaves and stems of control plants for the first harvest period weighed 137 g compared with average weights of 44 and 38 g for phenyl- and thidiazol-labeled groups, respectively.

   c) The study states that soybean fruit and sugarbeets were very small at maturity.

   If growing conditions in the study were not optimum, uptake of thidiazuron residues by rotational crops probably are not representative of field conditions.

4. The initial soil concentration for all crops and all treatments is stated as 0.2 ppm, but no data were submitted which verify the initial soil concentration.

5. There was no extraction of plant material after harvest because "low residue concentrations were expected." This prevented adequate characterization of residues in plant tissue. Residues present in concentrations down to 0.01 ppm or 10% of the applied rate, whichever is less, should be identified.

6. The study appendix describes a procedure which apparently could detect only intact thidiazuron (soybean and sorghum fruit were extracted with methanol). Although parent thidiazuron was not detected in soybean or sorghum fruit, it is possible that soil and/or plant metabolites of the parent compound were present but could not be detected by the method used.

7. It is not clear whether plant tissue and soil samples were stored before analysis. If they were stored, the duration and storage conditions were not reported. Frozen storage stability data were not presented.

8. The study report states that "Residues detected in roots are of no importance and have to be accepted with caution since during the growing season the roots were in direct contact with radioactive soil. Residues above the detection limit might be due to insufficient rinsing." The experimental techniques used should enable the researcher to distinguish between radioactive residues present as a result of uptake from those resulting from inadequate rinsing.

9. In soybean leaves and stems, the quantities of phenyl-labeled thidiazuron residues and thidiazol-labeled residues did not appear to differ substantially. In fruit (it is not clear whether "fruit" referred to seeds and pods or seeds alone), the highest residues observed (0.13 and 0.16 ppm) occurred for plants grown in soil treated with thidiazol-labeled thidiazuron.

10. The soil texture is reported as a loamy sand, but it is not possible to classify German soils according to the USDA soil classification system. The German and USDA systems are not directly comparable because the sand fraction (0.02-2mm) in the German system overlaps with the silt fraction (0.002-0.05mm) in the USDA system. The particle size breakdown should be reported according to the USDA system.

11. The study reports that "thin-layer chromatograms from early extractions showed a metabolite pattern not significantly different from that already observed in soil degradation studies." Evidence in support of this is not presented.

12. The concentration of thidiazuron in soil was reported as 0.2 ppm. Under field use conditions (the maximum application rate is 0.2 lb a.i./A) the expected concentration in the top 6 inches of soil would be 0.1 ppm. However, two applications of thidiazuron are allowed, but the total applied may not exceed 0.3 lb a.i./A, which translates to a theoretical soil concentration of 0.15 ppm. Further, thidiazuron does not degrade rapidly under field conditions, hence residues would be available for plant uptake throughout the growing season.

13. The study reports that "radioactivity decreased to about 0.10 ppm" in soil during the experiment. EFGWB does not agree that the evidence presented in Tables 13-18 supports this conclusion. Concentrations of radioactivity in soil do not appear to follow any demonstrable decline with time.

14. EFGWB does not necessarily concur with the study author's conclusion that "low amounts of radioactivity detected in plant parts at maturity could not be explained with the uptake of intact SN 49 537 (thidiazuron) from the soil." It is possible that intact thidiazuron was taken up and metabolized to other compounds within the plant, or that soil metabolites were taken up by the plants.

15. Soil cation exchange capacity (CEC) is reported as mVal/100g, which is the same as milliequivalents/100g (meq/100g). CEC should be reported as meq/100g or cmol(+)/kg.

Page_____ is not included in this copy.

Pages 158 through 176 are not included.

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____ Description of the product manufacturing process.

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DATA EVALUATION RECORD

STUDY 9

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CHEM 120301 Thidiazuron §165-1

FORMULATION--06--WETTABLE POWDER (WP)

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STUDY ID 41364908
Bruhl, R. 1982. W48 Thidiazuron: Residues of thidiazuron in rotational crops. Laboratory Project ID: R + S 24/82-PA 49 537.75/6. Unpublished study performed by Schering AG, Berlin, Germany, and submitted by Nor-Am Chemical Company, Wilmington, DE.

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DIRECT REVIEW TIME = 9

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28 APR 1993

CONCLUSIONS:

Accumulation - Confined Rotational Crops

1. The study provides supplemental information regarding the accumulation of thidiazuron residues in confined rotational crops.

2. [$^{14}$C]Thidiazuron residues accumulated in sugarbeets, sorghum, and soybeans planted 197 days (sugarbeets and sorghum), 306 days (soybeans), and 398 days (all crops) after loamy sand soil was treated with phenyl- or thiadiazol-labeled [$^{14}$C]thidiazuron at 0.2 ppm. Accumulation decreased as the length of the rotation increased. The concentrations of [$^{14}$C]residues in crops planted in soil treated with thiadiazol-labeled [$^{14}$C]thidiazuron were greater than in crops planted in soil treated with phenyl-labeled [$^{14}$C]thidiazuron. In crops planted in soil treated with phenyl-labeled [$^{14}$C]thidiazuron, residues were <0.01 ppm in sugarbeet tops and ≤0.02 ppm in roots; ≤0.02 ppm in sorghum stems, ≤0.01 ppm in fruit, and 0.02-0.04 ppm in roots; and ≤0.03 ppm in soybean stems and fruit and 0.01-0.07 ppm in roots. In crops planted in soil treated with thiadiazol-labeled [$^{14}$C]-thidiazuron, residues were ≤0.02 ppm in sugarbeet tops and ≤0.04 ppm in

roots; 0.01-0.04 ppm in sorghum stems, 0.01-0.03 ppm in fruit, and 0.03-0.08 ppm in roots; and 0.02-0.08 ppm in soybean stems, <0.01-0.07 ppm in fruit, and 0.03-0.11 ppm in roots. In the soil treated with phenyl-labeled [$^{14}$C]thidiazuron, total residues were 0.15 ppm immediately posttreatment, 0.12-0.13 ppm at 197-305 days, and 0.11-0.12 ppm at 398 days. In the soil treated with thiadiazol-labeled [$^{14}$C]thidiazuron, total residues were 0.18 ppm immediately posttreatment, 0.14 ppm at 197 days, 0.22-0.25 ppm at approximately 305 days, and 0.14 ppm at 566 days.

3. This study cannot be used to fulfill the data requirement for the following reasons:

(a) the study soil contained approximately 3.88% organic matter. U.S. cotton soils typically contain <1% organic matter. Thidiazuron may have been bound by the organic matter and therefore been unavailable for rotational crop uptake. Confined rotational crop studies should be carried out on soils typical of those on which the compound will be used.

(b) [$^{14}$C]residues in the crops and soil were not identified,

(c) storage stability data were not provided for the plant and soil substrates,

(d) the description of the experimental design was incomplete, and

(e) the test soil was incompletely characterized.

See Discussion for details.

4. It appears that new data are required. Because thidiazuron is used exclusively as a cotton defoliant, the new study should be conducted in U.S soils typical of cotton production and should incorporate rotational intervals and crops associated with cotton cultivation.

METHODOLOGY:

Samples (amounts unspecified) of dry loamy sand soil (42.4% coarse sand, 43.0% fine sand, 7.4% silt, 7.2% clay, 2.25% organic carbon, pH 6.6) were treated at 0.2 ppm with formulated (50% WP) uniformly phenyl-labeled $^{14}$C-thidiazuron or thiadiazol-labeled [5-$^{14}$C]thidiazuron (radiochemical purities >96%; specific activities 6.41 uCi/mg and 5.19 uCi/mg, respectively; sources unspecified). The soils were then moistened with water (final soil moisture content not reported), mixed in a cement mixer, and transferred to a plastic box. After 197 days of incubation (conditions unspecified), samples of the soil treated with phenyl- and thiadiazol-labeled [$^{14}$C]thidiazuron were separately placed in buckets (size unspecified) and planted to sorghum and sugarbeets (one crop per bucket). At 306 days posttreatment, additional buckets of treated soil were planted to soybeans. At 398 days posttreatment, buckets of treated soil were planted to sorghum, sugarbeets, and soybeans. (It could not be determined if any of the soils previously planted to crops were reused). Duplicate samples of

sorghum and sugarbeets were harvested twice when immature (50-66 and 92-108 days postplanting) and at maturity (sorghum at 159-168 days postplanting and sugarbeets at 168-178 days). Duplicate samples of soybeans were harvested when immature (twice following the 306-day rotation at 34 and 92-100 days postplanting and once following the 398-day rotation at 50 days postplanting) and at maturity (125-169 days postplanting). Upon sampling, the crop plants were separated into their various components. Three or five soil samples (size unspecified) were taken immediately posttreatment, prior to the 197-day rotation, and at all rotational crop harvest intervals. Storage conditions for the crop and soil samples were not described.

Plant samples were lyophilized and milled; subsamples were analyzed for total radioactivity by LSC following combustion. When plant components contained [$^{14}$C]residues >0.05 ppm, additional subsamples (10 g) were extracted with methanol using a magnetic stirrer for 20 minutes followed by a 2-hour reflux with methanol; aliquots of the extracts were analyzed for radioactivity using LSC. Unextracted [$^{14}$C]residues remaining in the extracted plant tissues were quantified by LSC following combustion.

Soil samples were lyophilized and milled; subsamples were analyzed for total radioactivity by LSC following combustion.

DATA SUMMARY:

[$^{14}$C]Thidiazuron residues accumulated in sugarbeets, sorghum, and soybeans planted 197 days (sugarbeets and sorghum), 306 days (soybeans), and 398 days (all crops) after formulated (50% WP) uniformly phenyl-labeled [$^{14}$C]-thidiazuron and thiadiazol-labeled [5-$^{14}$C]thidiazuron (radiochemical purities >96%) were applied at 0.2 ppm to loamy sand soil. Accumulation decreased as the length of the rotation increased; the concentrations of [$^{14}$C]residues in crops from the 197- and 306-day rotations (designated as Growing Period I by the study author) were approximately 1 to 3x greater than the concentration of [$^{14}$C]residues in crops from the 398-day rotation (designated as Growing Period II; Tables 5, 6, 10, 11, 15, and 16). The concentrations of [$^{14}$C]residues in crops planted in soil treated with thiadiazol-labeled [$^{14}$C]thidiazuron were approximately 1 to 4x greater than the concentrations of [$^{14}$C]residues in crops planted in soil treated with phenyl-labeled [$^{14}$C]thidiazuron.

In crops planted at 197 days posttreatment in soil treated with phenyl-labeled [$^{14}$C]thidiazuron, [$^{14}$C]residues at harvest were <0.01 and ≤0.01 ppm in mature sugarbeet tops and roots, respectively, and 0.01, 0.01, and 0.02-0.04 ppm in mature sorghum stems, fruit, and roots, respectively (Tables 5 and 10). In immature sugarbeets harvested at 66 and 108 days postplanting, [$^{14}$C]residues were <0.01 and 0.02 ppm in tops and roots, respectively; in immature sorghum harvested at 66 and 102 days postplanting, [$^{14}$C]residues were ≤0.01, 0.01, and 0.03 ppm in stems, fruit, and roots, respectively. In soybeans planted at 306 days posttreatment, [$^{14}$C]residues at harvest were 0.02, 0.02-0.03, and 0.06-0.07 ppm in mature stems, fruit, and roots, respectively; in immature soybeans harvested at

34 and 100 days postplanting, [$^{14}$C]residues were <0.01 and 0.01-0.07 ppm in stems and roots, respectively (Table 15).

In crops planted at 398 days posttreatment in soil treated with phenyl-labeled [$^{14}$C]thidiazuron, [$^{14}$C]residues at harvest were <0.01 ppm in mature sugarbeet tops and roots; ≤0.02, <0.01, and 0.03 ppm in mature sorghum stems, fruit, and roots, respectively; and 0.03,<0.01, and 0.04 ppm in mature soybean stems, fruit, and roots, respectively. In immature sugarbeets harvested at 50 and 92 days postplanting, [$^{14}$C]residues were <0.01 and ≤0.01 ppm in tops and roots, respectively; in immature sorghum also harvested at 50 and 92 days, [$^{14}$C]residues were ≤0.01, 0.01, and 0.02-0.03 ppm in stems, fruit, and roots, respectively; in immature soybeans harvested at 50 days, [$^{14}$C]residues were <0.01, <0.01, and 0.01 ppm in stems, fruit, and roots, respectively.

In crops planted at 197 days posttreatment in soil treated with thiadiazol-labeled [$^{14}$C]thidiazuron, [$^{14}$C]residues at harvest were ≤0.01 and 0.01 ppm in mature sugarbeet tops and roots, respectively; and 0.01-0.02, 0.02-0.03, and 0.02-0.03 ppm in mature sorghum stems, fruit, and roots, respectively (Tables 6 and 11). In immature sugarbeets harvested at 63 and 108 days postplanting, [$^{14}$C]residues were ≤0.02 and 0.01-0.02 ppm in tops and roots, respectively; in immature sorghum harvested at 63 and 102 days postplanting, [$^{14}$C]residues were 0.01-0.04, 0.02, and 0.03-0.08 ppm in stems, fruit, and roots, respectively. In soybeans planted at 306 days posttreatment, [$^{14}$C]residues at harvest were 0.06-0.08, 0.06-0.07, and 0.10-0.11 ppm in mature stems, fruit, and roots, respectively; in immature soybeans harvested at 34 and 92 days postplanting, [$^{14}$C]residues were 0.02-0.04 and 0.03-0.05 ppm in stems and roots, respectively (Table 16).

In crops planted at 398 days posttreatment in soil treated with thiadiazol-labeled [$^{14}$C]thidiazuron, [$^{14}$C]residues at harvest were 0.01 and <0.01 ppm in mature sugarbeet tops and roots, respectively; 0.03, 0.01-0.03, and 0.05 ppm in mature sorghum stems, fruit, and roots, respectively; and 0.05, <0.01, and 0.03 ppm in mature soybean stems, fruit, and roots, respectively. In immature sugarbeets harvested at 50 and 92 days postplanting, [$^{14}$C]residues were ≤0.01 and ≤0.04 ppm in tops and roots, respectively; in immature sorghum also harvested at 50 and 92 days, [$^{14}$C]residues were 0.01-0.02, 0.01, and 0.04-0.05 ppm in stems, fruit, and roots, respectively; in immature soybeans harvested at 50 days, [$^{14}$C]residues were 0.03, <0.01, and 0.03-0.04 ppm in stems, fruit, and roots, respectively.

In soybeans and sorghum grown on soil treated with thiadiazol-labeled [$^{14}$C]thidiazuron, methanol-soluble [$^{14}$C]residues ranged from 7.1 to 21.1% of the recovered radioactivity, an additional 30.6-51.3% was extracted with methanol under reflux, and unextracted residues ranged from 36.5 to 60.3% (Table 17). Crops grown on soil treated with phenyl-labeled [$^{14}$C]-thidiazuron were not extracted.

In the soil (depth/sample size unspecified) treated with phenyl-labeled [$^{14}$C]thidiazuron, total [$^{14}$C]residues were 0.15 ppm immediately posttreatment, 0.12-0.13 ppm at 197-305 days, and 0.10-0.11 ppm at 566 days (Table 18).

In the soil treated with thiadiazol-labeled [$^{14}$C]thidiazuron, total [$^{14}$C]-residues were 0.18 ppm immediately posttreatment, 0.14 ppm at 197 days, 0.20-0.25 ppm at 260-305 days, and ranged from 0.09 to 0.19 ppm between 340 and 566 days (Table 19).

DISCUSSION:

1. The soil used in this study, which apparently was a German soil, contained 2.25% organic carbon, which translates to approximately 3.88% organic matter (as a general rule, % organic matter = % organic carbon X 1.724). This soil is not representative of U.S. cotton soils which typically contain <1% organic matter. In this lab study, the soil organic matter may have bound thidiazuron, thereby reducing its availability for rotational crop uptake. Confined rotational crop studies should be carried out on soils typical of those on which the compound will be used.

2. Residues in the crops and soil were not identified.

3. Freezer storage stability data were not provided for the plant and soil substrates. For both plant and soil samples, the length of time from sampling to extraction was not reported and storage conditions were not described.

4. The test substance was formulated (50% WP) and, therefore, was not analytical grade or purer. The sources of the radiolabeled test substances were not reported.

5. The description of the experimental design was incomplete:

   a) the volumes of soil treated were not reported;

   b) it was not specified how the formulated test substance was prepared;

   c) it was not specified (soil moisture content, temperature, indoor or outdoor location) under what conditions the treated soil was aged;

   d) the size of the planting buckets and the volume of aged soil placed in each bucket were not specified;

   e) the number of each crop planted in the buckets was not reported;

   f) it could not be determined if any buckets of soil used for the 197- or 306-day rotations were reused for the 398-day rotations, or if sufficient soil was treated initially and aliquoted as needed for each rotation;

   g) it was not reported if the crops were grown indoors or outdoors;

   h) the size of the soil samples collected was not reported;

   i) it could not be determined if soybean "fruit" referred to beans plus pods or just the beans. Similarly, for sorghum, it was unclear if the

grain was separated and analyzed or if the entire panicle (inflorescence) was ground and combusted.

6. It was reported by the study author that the crops were planted after the treated soil had been aged for 1/2 and 1 year, and, that after the first rotation, the soil was mixed and once more transferred to buckets. The sorghum and sugarbeets were initially planted at 197 days (6.5 months) posttreatment, but soybeans were not planted until 306 days (10 months) posttreatment; sorghum, sugarbeets, and soybeans were planted at 398 days (13 months) posttreatment. From the study author's description, it appears that soil planted to the sorghum and sugarbeets for the 197-day rotation may have been reused for the 398-day rotation. However, this would not have been possible for the soybeans, because the soybeans planted at the 306-day rotation had not been harvested when the soybeans for the 398-day rotation were planted.

7. The loamy sand classification of the German soil could not be confirmed. The particle size scale used was not equivalent to the USDA scale; the sand fraction contained sand and silt particles. The particle size distribution reported by the study author was 42.4% coarse sand (0.2-2 mm), 43.0% fine sand (0.02-0.2 mm), 7.4% silt (0.002-0.02 mm), and 7.2% clay (<0.002 mm). The CEC of the soil was not reported.

8. A leafy vegetable crop, such as lettuce, mustard, or spinach, was not planted as a rotational crop. Cotton-vegetable rotations sometimes are used in California.

9. Air and soil temperatures were not reported.

10. Recovery efficiencies of phenyl- and thiadiazol-labeled [$^{14}$C]thidiazuron from fortified soil and plant samples were not provided.

11. All treatment-to-planting and planting-to-harvest intervals for the crops and sampling intervals for the soil were determined by the Dynamac reviewer using treatment and sampling dates provided in Tables 2, 7, and 12.

12. The study author reported that the soybeans were stunted and believed that the growing conditions (soil, planting vessel, light conditions) were not adequate. No control crops were grown for comparison, nor was sufficient information provided regarding crop growing conditions. Pesticide uptake by crops should be measured only in healthy plants.

13. To meet the study's purpose, the pesticide should be aged under aerobic conditions in the soil for a time approximating the anticipated agricultural practice. In this study, rotational intervals of 195, 306, and 398 days were chosen, but the rationale for choosing these intervals was not explained. Data for a 30-day rotation should be provided to assess possible accumulation in a winter crop planted after cotton harvest. (In some cropping systems, cotton is followed by wheat, alfalfa, or a winter forage.) The 30-day rotation study should be conducted on a typical cotton soil.

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