

US EPA ARCHIVE DOCUMENT



Shaughnessy No.: 120301

Date Out of EFGWB:

12/16/89

To: R. Whitters  
Product Manager PM #50  
Registration Division (H7505C)

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

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

Attached, please find the EFGWB review of...

Reg./File # : \_\_\_\_\_

Chemical Name : Thidiazuron

Type Product : Herbicide

Product Name : W63-Thidiazuron

Company Name : NOR-AM Chemical Company

Purpose : Review of data submitted in response to registration standard and response to initial registration standards.

Action Code : 660 EFGWB #(s) : 90737

Date Received : 8/28/89 Total Reviewing Time : 4 days

Deferrals to:  Ecological Effects Branch  
 Dietary Exposure Branch  
 Non-Dietary Exposure Branch  
 Toxicology Branch I  
 Toxicology Branch II

1.0 CHEMICAL:

chemical name: N-phenyl-N'-1,2,3-thiadiazol-5-yl urea

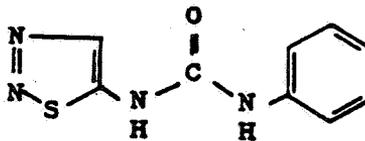
common name: thidiazuron

trade name: W63-Thidiazuron

structure:

CAS #:

Shaughnessy #: 120301



2.0 TEST MATERIAL: discussed in DER

3.0 STUDY/ACTION TYPE: Review of registration standards for aqueous photolysis study and response to registration standards.

4.0 STUDY IDENTIFICATION:

Brehm, M., W63-Thidiazuron: The Photodegradation of Thidiazuron in Aqueous Solutions. performed by Schering AG, Federal Republic of Germany, sponsored and submitted by NOR-AM Chemical Company. dated 5/23/89. received EPA 8/28/89, MRID 411882-1.

5.0 REVIEWED BY:

James A. Hetrick, Ph.D.  
Chemist, ECRS # 1  
EFGWB/EFED/OPP

Signature: *James A. Hetrick*

Date: 12/6/89

6.0 APPROVED BY:

Name: Paul Mastradone, Ph.D.  
Section Chief, ECRS # 1  
EFGWB/EFED/OPP

Signature: *Paul J. Mastradone*

Date: 7-8-89

7.0 CONCLUSIONS:

7.1 Satisfaction of Data Requirements

EFGWB concludes the aqueous photolysis study (161-2) cannot be used to satisfy the data requirements for the following reasons:

1. The mercury (Hg)-arc light experiments are not acceptable because the spectral distribution of light is not continuous and, the light intensity is approximately 3.5 times greater than natural light.
2. There were inconsistent light sources used between the photodegradation rate and degradate identification studies.

3. The identification for photodegradates (>10%) did not provide definitive characterization of the compounds.

Although the study is unacceptable, EFGWB concludes that thidiazuron is rapidly photodegraded in aqueous environments. Thidiazuron appears to be stable to hydrolytic degradation in buffered (pH 5, 7, and 9) aqueous environments. Limited information from the studies show photodegradates differ with solution pH; however, only qualitative structural analysis indicate the photodegradates retain the parent phenyl-urea compound.

#### 8.0 RECOMMENDATIONS:

Inform the registrant of the data deficiencies identified in the aqueous photolysis study which do not satisfy the data requirements. Specific deficiencies are listed in the aqueous photolysis data evaluation review.

#### 9.0 BACKGROUND:

The status of data requirements are as follows:

hydrolysis -- Accepted  
photolysis in water -- Not accepted  
soil photodegradation -- Accepted  
aerobic soil metabolism -- Not accepted  
anaerobic soil metabolism -- Not submitted  
leaching/adsorption/desorption -- Not accepted  
terrestrial field dissipation -- Not submitted  
confined accumulation on rotational crops --  
fish bioaccumulation --

#### 10.0 DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

NOR-AM responded to EFGWB review comments concerning the aerobic metabolism and leaching/adsorption studies submitted on January, 4 1986.

##### 10.1 Aerobic Metabolism Study

EFGWB Comment: The EFGWB data review on November 28, 1986 found an unexplained discrepancy for the thidiazuron half-life (118 days) between submitted experiments. The experimental procedures for the two aerobic metabolism experiments were similar; however, the soil handling procedures were vague for each experiment. The EFGWB review requested that NOR-AM explain the soil handling procedures to confirm the thidiazuron metabolism half-life.

NOR-AM Response to Comment: The NOR-AM Chemical Company stated the aerobic metabolism studies were conducted with the same German standard soil; however, the soil preparation procedures differed between experiments. In the first experiment (W26), the soil (1.85% C and CEC 4.6 mVal 100g<sup>-1</sup> soil) was sieved moist and stored in presumably open plastic bags for 632 days. The soil (2.36% C and CEC 11.2 mVal 100g<sup>-1</sup> soil) used in the second experiment (W25) was "biologically activated" by planting alfalfa prior sampling; thereafter, the soil was sieved moist and stored for only 30 days. NOR-AM concluded the second study (W25) is probably more representative of field conditions because the soil was "biologically activated" prior to experimentation.

EFGWB Comment to Response: EFGWB concludes the soil metabolism studies do not provide a reliable half-life estimate for thidiazuron stability in soil. The soils used in these studies were poorly characterized for both their chemical and physical properties. In particular, the soil properties are not expressed in standard USDA units and there is no soil taxonomic description for the German standard soil. EFGWB is uncertain that mVal/100 g are equivalent units to the standard CEC units of meq/100g. Furthermore, soil properties are not static during storage and therefore can change with both sampling time and preparation procedure. EFGWB concludes there is a problem in resolving the half-life for thidiazuron stability from these experiments. Therefore, EFGWB recommends the aerobic metabolism study be repeated using a U.S. agricultural soil from an area typically exposed to thidiazuron.

## 10.2 Mobility and Absorption of Thidiazuron

EFGWB Comment: The EFGWB review on November 26, 1986 accepted the seven leaching studies and absorption study for screening/review. The EFGWB review requested that a companion desorption study be done to complete the absorption study data requirements.

NOR-AM Response to Comment: The NOR-AM Chemical Company did not provide any desorption study for thidiazuron as requested by the EFGWB review. NOR-AM concluded the seven leaching studies consistently showed that thidiazuron was immobile in soil. In addition, the adsorption study revealed that thidiazuron has a high Koc (500-900). Hence, NOR-AM feels that thidiazuron is not a potential leacher.

EFGWB: Comment to Response: The seven leaching studies show that neither thidiazuron or its degradates leached beyond a 6 cm depth. In fact, more than 80% of the thidiazuron or its degradates were found in the surface 4-6 cm of soil. In addition, the adsorption study showed that thidiazuron had a high absorption coefficient K (K=21.3, Koc=900) for a loamy sand soil (German standard soil); however, there was very little thidiazuron absorption (K=2.2; Koc=600) in a river sand. In addition, there were no leaching studies conducted on the river sand to provide a

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worst-case scenario. EFGWB concludes that a companion desorption study would not provide additional information pertaining to the leaching potential as proposed in the SEP 163-1. Therefore, the leaching/absorption studies are accepted as satisfying the data requirements.

11. COMPLETION OF ONE-LINER:

12. CBI APPENDIX: attached to individual DERS

DATA EVALUATION REVIEW

I. Study Type: Aqueous photolysis

II. Citation: Brehm, M., W63-Thidiazuron: The Photodegradation of Thidiazuron in Aqueous Solutions. performed by Schering AG, Federal Republic of Germany, sponsored and submitted by NOR-AM Chemical Company. dated 5/23/89. received EPA 8/28/89, MRID # 411882-1.

III. Reviewer:

Name: James A. Hetrick, Ph.D., Chemist  
Title: Environmental Chemistry Review Section #1  
Organization: EFGWB/EFED/OPP

*James A. Hetrick*  
12/6/89

IV. Approved by:

Name: Paul J. Mastradone, Ph.D., Chief  
Title: Environmental Chemistry Review Section #1  
Organization: EFGWB/EFED/OPP

*Paul J. Mastradone*

V. Conclusions:

EFGWB concludes this study is scientifically sound but it cannot be used to satisfy the data requirements for the following reasons:

1. The mercury (Hg)-arc light experiments are not acceptable because the spectral distribution of light is not continuous and, the light intensity is approximately 3.5 times greater than natural light.
2. There were inconsistent light sources used between the photodegradation rate and photodegradate identification studies.
3. The structural identification for photodegradates did not provide definitive characterization of specific compounds.

Based on this supplemental data, thidiazuron has a short photolysis half-life ranging from 32 to 49 min<sup>-1</sup> for buffered aqueous solutions. The identification of photolysis degradates suggest that solution pH regulated the degradate end-product. Structural photodegradate identification show the phenyl-urea parent compound is retained in both degradates; however, the chemical properties were different between degradates. Based on the results of this study, EFGWB tentatively concludes that thidiazuron will not persist in aqueous environments exposed to natural light.

## VI. Materials and Methods:

### A. Hg-Arc

The photolysis experiments were conducted using a double-filtered (e.g., borosilicate and quartz filter) mercury (Hg)-arc light with an integrated light intensity of  $0.91 \text{ mWatt cm}^{-2}$  in the 290-320 nm wavelength range. Unlabelled thidiazuron buffered solutions containing  $10 \text{ ug ml}^{-1}$  thidiazuron were prepared using a 1% acetonitrile/D\*H<sub>2</sub>O solvent in the appropriate buffer solutions (e.g., acetate, phosphate, and borate). The thidiazuron buffer solutions were placed in heat-treated quartz vials and exposed to light for 0, 2, 5, 10, 15, 20, 30, 40, and 60 minutes. The temperature was held nearly constant at  $27 \pm 2^\circ\text{C}$ . After light exposure, the remaining thidiazuron in solution was determined in a MeOH/phosphate (pH=7) eluent using a HPLC (HP 1090L) equipped with a filter photometer detector set at 210 nm. The thidiazuron first-order rate constant was estimated using linear regression.

HPLC Calibration Curve (Unlabelled thidiazuron, pH 5)

$$\text{Peak Area} = 266.20 + 972.96 * (\text{thidiazuron, ug ml}^{-1}) \quad R^2 = 0.9995$$

$$\text{Range of Standards low} = 1.00 \text{ ug ml}^{-1}$$

$$\text{high} = 10.00 \text{ ug ml}^{-1}$$

First-Order Rate Constant Estimation (Unlabelled thidiazuron, pH 5)

$$\text{LnC} = 4.6163 - 0.0525 * (\text{time}) \quad R^2 = 0.9995$$

### B. Quantum Yield Experiment

The photolysis half-life was calculated using quantum degradation efficiency estimates (molecules degraded/photon absorbed) in conjunction with the Hg-arc light intensity distribution. The absolute light intensity distribution for the Hg-arc lamp was measured using an actinometric procedure, 0.01 M uranyl sulfate and 0.05 M oxalic acid, with a constant quantum yield of 0.56 in the 290-500nm wavelength range. Therefore, the overlap of the thidiazuron light absorption spectra and absolute light intensity provide an estimate of the photons absorbed by thidiazuron. The photolysis rate constants were calculated using a photochemical efficiency equation.

### C. Computer Simulation (GCSOLAR)

Thidiazuron aqueous photolysis rates were estimated using computer generated light intensities. The simulated environmental conditions represented midseason conditions with solar declinations from +20 to -10 at latitudes of 30, 40, and 50° N. The photolysis rate constant was calculated using the quantum yield estimate (i.e., determined in the quantum yield experiment) multiplied by the rate of light absorption for thidiazuron.

#### D. Natural light

Buffer solutions containing 10 ug ml<sup>-1</sup> unlabelled thidiazuron were placed in heat-treated quartz vials and exposed to natural light for 0, 15, 30, 60, 90 minutes. The vials were exposed to sunlight at 11:00 am on March 28, 1989 under clear skies with an integrated energy of 58.2 mWh cm<sup>-2</sup>. After light exposure, the remaining thidiazuron in solution was determined using HPLC. The rate constant was calculated assuming first-order kinetics using linear regression.

#### E. Degradate Determination and Material Balance

Thidiazuron photolysis degradate identification and quantification was assessed using Hg-arc irradiated radiolabelled thidiazuron solutions and HPLC reference compounds. Degradate formation was assessed as a function of time using a similar experimental procedure as described for the Hg-arc photolysis studies. The specific activity of thidiazuron was quantified using both HPLC (equipped with a variable wavelength monitor and radioactivity detector) and LSC. The quantity of thidiazuron and degradates were assessed using the initial <sup>14</sup>C solution specific activity as a 100% index. Further characterization of the degradates included degradate synthesis using Xenon irradiated thidiazuron solutions; thereafter, degradates were concentrated and purified for structural analysis with NMR/IR/MS.

Test compounds: thidiazuron unlabelled, 98.9 w/w purity; thidiazuron <sup>14</sup>C labelled at the fifth carbon of the thiadiazol ring, specific activity 2.5 MBq mg<sup>-1</sup>, purity 98%; thidiazuron <sup>14</sup>C-labelled [-U-<sup>14</sup>C] attached to the phenyl group, specific activity 11.8 MBq mg<sup>-1</sup>, purity 98%.

HPLC Reference Compounds: 5-amino-1,2,3 thiadiazole; N-phenyl-N'-1,2,5-thiadiazol 3-yl urea; N,N - diphenyl urea; N-phenyl urea; N-phenyl urethane.

#### VII. Study Author's Results and/or Conclusions:

A. The absorption spectra of thidiazuron has maximum light absorption at a wavelength of 298nm in pH 5 and 7 buffered solutions (Figure 1). In contrast, maximum light absorption in pH 9 buffer solution occurs at 327 nm. The shift in thidiazuron spectral properties with pH was attributed to ionization (i.e., pKa=8.8).

B. The first-order rate constant for aqueous photolysis using Hg-arc irradiation was similar to natural light when corrected for light intensity differences in the wavelength range of 290-320 nm (Tables 1 and 2). The average corrected half-life of thidiazuron under Hg-arc and natural light was 37.1 and 41.8 min<sup>-1</sup>, respectively.

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C. Thidiazuron was stable in the buffered solutions suggesting hydrolysis did not account for degradate formation (Table 3).

D. The average quantum-yield for thidiazuron degradation in aqueous environments is 0.075 molecules degraded photon<sup>-1</sup> (Table 4).

E. The material balance using radiolabelled thidiazuron was between 100-105% (Table 5).

F. Degradate identification studies show that at least two products formed during Hg-arc light irradiation. The mass balance calculations suggest solution pH regulated the degradate formation. In slightly-acidic solutions (pH 5), the predominate degradate (i.e., 72% of the original mass) had an HPLC retention time of 16 minutes (Table 5, Figure 2). In contrast, the predominate degradate (i.e., 64% of the original mass) in neutral and alkaline solutions (pH 7 and pH 9) had a HPLC retention time of 2.5 minutes. The radioactive tracing experiments suggest both degradates retained the phenyl and fifth carbon of the thiadizol group of the parent urea compound after photolysis (Figure 3). Further identification using NMR/IR/MS suggest the degradate formed in neutral and alkaline solutions retained only the phenyl-urea parent compound.

#### VIII. Reviewer's Comments:

A. The Hg-arc experiments are not acceptable because the spectral distribution of light is not continuous and, the light intensity is approximately 3.5 times greater than natural light. The commonly accepted artificial light source for photolysis experiments is Xenon because it has a continuous spectral distribution of light and, the normalized photon irradiance simulates natural light over a broad wavelength range (i.e., 250-410 nm).

B. There were inconsistent light sources used between the photodegradation rate and photodegradate identification studies. The photolysis rate experiments were conducted under Hg-arc light and natural light; however, the degradate identification experiment was conducted under a Xenon light source. There should be a consistent light source (e.g., natural light or Xenon lamp) used for both the photolysis rate and degradate identification experiments.

C. The exact structural identification is necessary for photodegradates exceeding 10% of the mass balance. The photodegradates, representing HPLC peak 1 and 3, are only partially identified as retaining the parent urea-phenyl compound.

D. Photolysis half-life estimates calculated from computer generated light intensities (i.e., GCSOLAR) are not accepted in lieu of experimental results. Therefore, model simulations are considered strictly supplemental and cannot be used in the data evaluation review.

IX. CBI Appendix

Thidiazuron environmental fate review

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The material not included contains the following type of information:

- Identity of product inert ingredients
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  - Description of the product manufacturing process
  - Description of product 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
  - FIFRA registration data
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