

FILE COPY

Date Out EFB: OCT 9 1981

To: Product Manager 23 Mountfort
TS-767

From Dr. Willa Garner *WJ*
Chief, Review Section No. 1
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 2139-REE

Chemical: Thidiazuron

Type Product: Herbicide

Product Name: DROPP

Company Name: Nor-AM

Submission Purpose: Use as defoliant on cotton

ZBB Code: 3(c)(7)?

ACTION CODE: 110

Date in: 6/12/81

EFB # 870

Date Completed: OCT 9 1981

TAIS (level II)

Days

Deferrals To:

61

21

____ Ecological Effects Branch

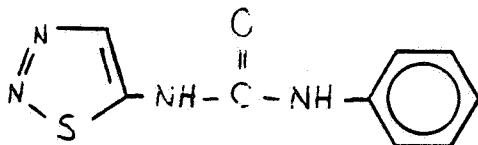
____ Residue Chemistry Branch

____ Toxicology Branch

1. INTRODUCTION

1.1 This is a request by Nor-Am for the registration of thidiazuron on cotton as a defoliant. According to EFB records, this is the first registration request for this chemical; however, EUP requests have been received and reviewed in the past.

1.2 Structure and name



5-N-phenylcarbamoylamino-1,2,3,4-thiadiazole or SN 49537.

1.3 Chemical and physical properties (See review dated Aug. 9, 1976)

v.p. = 3×10^{-11} Torr (25 °C)

molecular weight - 220.2

m.p. - 213 °C with decomposition

solubilities - water	20 ppm
methanol	0.45 g/100 ml
acetone	0.8 g/100 ml
chloroform	13 ppm
benzene	35 ppm
hexane	6 ppm
DMF	>50 g/100 ml

2. DIRECTIONS FOR USE

- 2.1 Apply 0.1-0.2 lb ai/A by ground or air. Use the higher rate during periods of low temperatures. Apply to mature cotton plants when 70% or more of the bolls are open. Apply at least 5 days prior to anticipated picking.
- 2.2 Two applications (not exceeding a total of 0.3 lb ai/A) may be necessary to defoliate rank cotton.
- 2.3 Preconditioning with 0.005 - 0.025 lb ai/A may aid in the defoliation process. For preconditioning, apply to mature cotton plants 1-2 weeks before the main application when 70% or more of the bolls are open.

- 2.4 Do not use when the average 24 hour temperature is expected to be below 70 °F for 2-3 days after application because defoliation may be substantially reduced.

3. DISCUSSION OF DATA

- 3.1 Determination of Hydrolysis Rate of 5-N-phenylcarbamoylamino-1,2,3-thiadiazole, Dr. Riemann, March 17, 1975, Report No. APC 11/75, Acc. No. 070132, Appx. 1.

Procedure

SN 49537 was dissolved in water of about 30 ppm and subjected to severe conditions of pH and temperature. The aqueous solution was analyzed for parent by extraction and TLC.

Results

- 1) No decomposition occurred during 24 days in 1N NaOH solution at room temperature.
- 2) No decomposition occurred during 3 hours of reflux in 1N HCl.
- 3) Complete hydrolysis was noted after 3 hours of refluxing in 1N NaOH.

Conclusions

SN 49537 is stable to severe conditions of hydrolysis.

- 3.2 Hydrolysis of SN 49537 (preliminary report), Dr. Repenthin, Berlin, May 11, 1976, Acc. No. 070132, Appx. 2, (additional data to report APC 11/75 reviewed above in section and Appx. 3, APC 26/79.

Procedure

A solution was prepared containing 996 ml of 1N NaOH and 4 ml of a methanolic solution of SN 49537 resulting in a solution of 112.2 umoles SN 49537 per liter. This solution was incubated at 50 °C for 575.5 hours with sampling.

Results

<u>Sample #</u>	<u>Hours incubated</u>	<u>SN 49537 (umoles)</u>
1	0	112.2
2	19.25	93.8
3	42.92	88.6
4	66.42	76.0
5	94.42	70.3
6	502.58	14.4
7	527.25	14.4
8	550.75	9.4
9	572.50	11.0
10	575.50	11.3

Conclusion

- 1) The hydrolysis constant (k) for SN 49537 at pH=14 and 50 °C was 3.93×10^{-3} hour⁻¹. This corresponds to a halflife of 7.35 days at the above conditions.
- 2) From the above data halflife values at pH 5, 7 and 9 are estimated to be about 2×10^7 , 2×10^5 and 2×10^3 years at 50 °C, respectively.

3.3 *hydrolysis* Photolysis of SN 49537, Dr. Buhmann, Berlin, May 12, 1976
Acc. No. 070132, Appx. 4.

Procedure

A solution of SN 49537 (116 mg/4.3 l) in deionized water was exposed to radiation from a high pressure mercury lamp with light <290 nm filtered out. Irradiation was at 25-26 °C (1.7×10^6 erg/cm² at 600W) for one hour. The irradiated solution was then extracted and examined by TLC followed by MS.

A similar experiment was conducted under nitrogen at 25 °C and 1.4×10^6 erg/cm² at 500 W for 45 minutes.

A third experiment was run using tap water as the solvent and under a stream of synthetic air at 1.7×10^6 erg/cm² at 600 W.

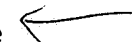
Finally, an experiment was run in tap water and acetone (about 20%) added as a photosensitizer at 1.7×10^6 erg/cm² at 600 W.

4

Results

Degradation occurred during the 1 hour of irradiation in each of the 4 experiments. Only 1 product formed in the first 3 experiments and is an isomer of the parent compound of unknown structure. In the presence of acetone additional polar compounds were formed.

Conclusions

SN 49537 will isomerize, in part, under exposure to light in aqueous systems to an isomer of undetermined structure. In the presence of acetone, polar compounds are formed in addition. 

- 3.4 Photolysis of SN 49537, Report Number APC 30/76, Dr. Buhmann, Berlin, June 25, 1976, Acc. No. 070132, Appx. 5.

Procedure

Two solutions of SN 49537 were prepared in deionized water, resulting in concentrations of 15.9 and 23.5 ppm SN 49537.

The solutions were irradiated from an artificial light source at 700 W and 1.95×10^6 erg/cm² with radiation <290 nm filtered out.

Samples were taken during the 5 1/2 hours irradiation and analyzed by LC.

Results

- 1) The halflife of the parent compound was 10-15 minutes and degraded at a rate of $K_1 = 0.038 \text{ min}^{-1}$.
- 2) A photoproduct of undetermined structure formed and is an isomer of the parent. It too degraded with a rate $K_2 = 0.004 \text{ min}^{-1}$.

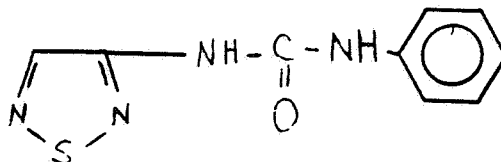
Conclusion

SN 49537 is subject to photolysis. An isomer of the parent is formed which in turn further degrades.

- 3.5 Photochemical Behaviour of Thidaizuron in Aqueous Solution, V. Buhmann, Berlin, Acc. No. 070132, Appx. 6.

Comments

The authors considered various mechanisms of rearrangement and degradation of SN 49537 and concluded that the isomer of SN 49537 that forms due to light has the following structure.



That conclusion was supported by subsequent synthesis of the isomer.

Refer to the photo studies in sections 3.7 and 3.8.

3.6 Preliminary Description of the Equipment for the Photolysis of Agricultural Chemicals on Soil Surfaces, Acc. No. 070132, Appx. 7.

Comments

This material is a description of the experimental method used in the soil photolysis study reviewed in section 3.7, below.

A xenon arc lamp with a filter to remove wavelengths <290 nm with a reflector behind the lamp was used. The radiation energy of the filtered light was 2080 W/m².

Standard soil 2.3 (Speyer) was spread on TLC plates to 0.5 mm and the soil thin layer was then divided into an array of 30 separate sections (3 x 4 cm each) by scraping away the soil from around each section. The sections were treated with ¹⁴C-SN-49537 and exposed to light. Via air-cooling and water - cooling, the soil surface will not exceed 30 °C. Also, there are traps for volatile products. After exposure to light, the soil sections are extracted and analyzed, via standard chromatographic and LSC techniques.

3.7 Photodegradation of Thidiazuron (SN 49537) on Soil Surfaces (Preliminary Report), Dr. M. Klehr, December 2, 1979, Acc. No. 070132, Appx. 8.

Procedure

Refer to the description of the experimental design in section 3.6 above.

Each of six sections of the soil TLC plate were treated at an equivalent rate of 150 gm/ha with ^{14}C -SN-49537 (site of radio-labeling not given). After light exposure, the soil sections were scraped and extracted with MeOH. The extract was analyzed by TLC and the extracted soil was combusted.

Light exposure was either for a period of 2 or 3.75 hours.

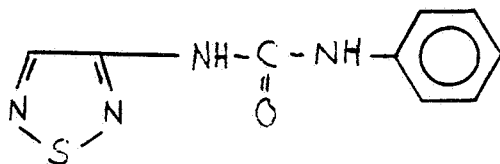
Results

1) No volatilization of radiolabeled material was detected.

2) Results of Photolysis of SN 49537

<u>Exposure time</u> <u>hours</u>	<u>Covered</u> <u>Uncovered</u>	<u>Unextractable</u> <u>%</u>	<u>Extractable</u>		
			<u>Parent</u>	<u>Product #2</u>	<u>Polar</u>
2	unc.	22.8	49	23	3
2	c.	15	88.3	-	-
3.75	unc.	27.4	31.5	36.1	6.1
3.75	c.	14.0	90.7	-	-

3) Structure of "product #2"



Conclusions

1) SN 49537 will photolyze on soil surfaces forming the isomer (of the parent) known as photoproduct #2. The photolytic half-life of the parent compound is about 2 hours.

2) Small amounts of unidentified polar compounds also form during photolysis.

3.8 Hydrolytic and Thermal Stability of the Photoproduct of SN 49537,
Dr. Repenthin, APC 03/77, January 24, 1977, Acc. No. 070132, Appx. 9.

Comments

- 1) The photoproduct of SN 49537, known as photoproduct #2, did not degrade after 4 hours and 90 °C at pH 1 or pH 14.
- 2) The water solubility of the photoproduct #2 was determined to be 41-46 mg/liter. ←
- 3) The photoproduct #2 decomposed 10% after 54 days at 120 °C.

3.9 Mobility SN 80178 ("Photoproduct" of Thidiazuron) in Four Soils, Dr. Bruhl, December 5, 1978, Acc. No. 070132, Appx. 10.

Procedure

Four different soils, described below, in Table 1, were treated with ¹⁴C-SN 80178 (photoproduct of thidiazuron), 1-[UL-¹⁴C]-phenyl-3-(1, 2,5-thiadiazol-3-yl) urea at a rate equivalent to 0.24 kg ai/ha.

Four columns were used for each soil (3 reps and 1 control), and were 30 cm high x 5 cm id. The columns were filled with 2 mm? sieved soil, treated with the SN 80178 and eluted with deionized water at 7-10 ml per hour over 6 days. This is equivalent to 85-120 mm of rain per 24 hours.

Percolated water was analyzed daily for ¹⁴C activity and the soil column was sectioned, after elution, into two 5 cm and two 10 cm segments which were extracted with methanol. The methanol was analyzed for ¹⁴C activity and the extracted soil was combusted.

Results

- 1) Speyer soil - About 1.6-2.4% of the initial activity leached. About 10% was not recovered and was probably lost as CO₂.
- 2) Neuhausen soil - About 0.2% of the initial activity leached. About 10-20% was lost probably as CO₂.
- 3) Californian loamy sand - About 0.7% of the initial activity leached. About 93-100% of the initial activity was recovered and was principally in the top 5-10 cm.
- 4) Mixture TKS 2/compost soil - Less than 0.1% of the initial activity leached with >95% of the applied remaining in the top 5 cm.

Conclusions

SN 80178 not leach.

Table 1 Characterization of soils

used in section 3.9 of this report

Soil type	German standard soil 2.1 "Speyer"	German standard soil 2.2 "Neuhofen"	Californian loamy sand	Mixture TKS 2/ compost soil
pH	6.6	5.7	5.2	6.0
Organic C	0.475	1.930	1.120	4.040
Clay (<2 _{um})	3.5)	7.3)	4.1)	7.2)
Silt (2 - 20 _{um})	2.6)	6.5)	7.5)	7.5)
Fine sand (20 - 200 _{um})	23.4)	29.0)	54.6)	53.3)
Coarse sand (0.2 - 2 mm)	70.5)	57.2)	33.8)	32.0)
Cation exchange capacity	2.2	7.8	5.0	11.7
Max. waterholding capacity	24	30	30	66

3.10 Degradation of SN 80178 (Photoproduct of Thidiazuron) in an Activated Loamy Sand, Dr. Bruhl, Berlin, January 20, 1980, Acc. No. 070132, Appx. 11.

Procedure

German standard soil 2.2 (Neuhofen), described below:

pH	6.6
organic C %	2.36
clay (<2/um)	5.0
silt (2 - 20/um)	8.3
fine sand (20 - 200/um)	32.6
coarse sand (0.2 -2 mm)	54.1
cation exchange capacity (mVal/100 g)	11.2
max. waterholding capacity (g H ₂ O/100 g)	36

was biologically activated by growing alfalfa on it for 4 weeks before fortification with SN 80178. Soil samples of 50 gm were fortified with 0.11 mg of SN 80178 (labeled in the phenyl ring).

Soil aliquots were taken periodically for about a year, extracted, analyzed by TLC and combusted.

Results

1) Extraction of SN 80 178 from a loamy sand. Aerobic study

Soil type: German standard soil 2.2 ("Neuhofen")
 Applied product: 0.11 mg a.i./sample ($\hat{=}$ 2.2 mg a.i./kg soil)
 Applied radioactivity: 3.21×10^5 dpm/sample
 Specific radioactivity: 4.86×10^5 Dq/mg $\hat{=}$ 2.92×10^7 dpm/mg
 Values are expressed in % of applied product.

Day	$^{14}\text{CO}_2$	Organic solvent extraction	Alkali extraction		Combustion	Total
			$\Sigma =$	Fulvic + Humic ac.		
0	-	90.4	0.5	0.2	0.3	94.1
12	8.2	70.3	6.5	3.2	3.3	96.6
21	18.0	49.0	10.6	4.9	6.1	94.3
56	41.0	18.7	13.5	5.8	7.8	87.9
105	52.8	14.4	13.1	4.7	8.6	91.6
180	58.3	14.2	11.4	3.9	7.8	93.6
264	62.6	12.4	10.0	3.3	6.8	93.9
359	66.9	7.9	9.2	2.9	5.7	95.1

2) Breakdown of SN 80 178 in a loamy sand under aerobic conditions

Soil type: German standard soil 2.2 ("Neuhofen")
 Applied product: 0.11 mg a.i./sample ($\hat{=}$ 2.2 mg a.i./kg soil)
 Applied radioactivity: 3.21×10^5 dpm/sample
 Specific radioactivity: 4.86×10^5 Bq/mg $\hat{=}$ 2.92×10^7 dpm/mg
 Values are expressed in % of applied product.

Day	$^{14}\text{CO}_2$	SN 80 178	Origin	Unknowns				Bound residues	Total
				I	II	III	Other		
0	-	89.2	0.2	-	-	0.5	0.5	3.7	94.1
12	8.2	68.6	0.4	0.4	0.7	0.3	-	18.1	96.7
21	18.0	47.3	0.5	0.4	0.4	0.5	-	27.3	94.4
56	41.0	17.8	0.4	0.2	0.2	0.1	0.2	28.2	88.1
105	52.8	13.0	0.6	0.2	0.1	0.1	0.4	24.4	91.6
180	58.3	13.7	0.2	0.3	-	-	-	21.1	93.6
264	62.6	11.3	0.5	0.1	0.1	0.1	0.3	18.9	93.9
359	66.9	7.0	0.3	0.1	0.1	0.1	0.3	20.3	95.1
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$R_f \times 100$		63		5	32	56	Acetone/ethyl ether, 1+1(v/v)		
		77		9	43	59	Ethyl acetate/DMPA*, 9+1(v/v)		

*Dimethylformamide

Conclusions

- 1) SN 80178 will degrade in soil under aerobic conditions with a halflife of about 3 weeks. The release of CO₂ indicates degradation of the phenyl moiety.
- 2) Bound residues peak at about 30% of the applied at 5 weeks but slowly dissipate thereafter.
- 3) At least 3 unknowns were found with one being tentatively identified as N-phenylurea. None of the degradation products ever reached a level greater than 0.7% of the applied.

3.11 Report on Degradation of SN 49537 in Soil, Dr. Bruhl, Berlin, July 17, 1980, find report, Acc. No. 070132, Appx. 12. Aerobic and Anaerobic Soil Degradation.

Procedure

German standard soil 2.2 Neuhofen (pH = 6.8, organic C = 1.85%, clay <2 u = 9.3%, silt 2-20 u = 6.5%, CEC = 4.6 mVAL per 100 gm) was fortified to 2 ppm with ¹⁴C-SN 49537 [N-(UL-¹⁴C)-phenyl-N'-(1,2,3-thiadiazole-5-yl)-urea]. The soil was moistened to 86% and then incubated in biometer flasks in the dark at 25 °C. ¹⁴CO₂ product was monitored and soil samples were taken for up to a year.

The soil was extracted and separated into humic and fulvic acids with TLC analysis of the extracts and combustion of the extracted soil.

In the anaerobic study, 30 day old samples from the aerobic study were flooded with deoxygenated water and aged anaerobically for 120 days. The soil was extracted and the water was partitioned followed by standard methods of radioanalysis.

Results

Table 1 Results of extraction and combustion of soils in % of applied dose

Under aerobic conditions

Column	2	3	4	5	6	7	8	9
Day	$^{14}\text{CO}_2$	Organic solvent extraction (CH_3) ₂ CO/ CH_3OH Soxhlet	Residues bound to humic and fulvic acids = fulvic + humic			Combustion	Total	
0	-	91.1	7.0	-	-	3.5	101.6	
7	0.1	63.9	12.3	15.7	5.3	7.6	99.6	
14	0.2	58.7	14.9	18.0	7.6	8.5	100.3	
30	0.9	51.0	20.3	17.4	8.0	12.4	102.0	
60	2.1	49.6	13.9	19.3	8.3	13.7	98.6	
91	4.9	41.2	15.7	24.0	9.6	15.2	101.0	
182	12.2	31.6	13.7	24.7	12.3	14.2	96.4	
360	27.0*	18.2	10.5	24.6	13.1	18.5	98.8	

*The lowest $^{14}\text{CO}_2$ production found in a replicate was 19% at 360 days.

Table 2 Conversion of SN 49 537 in "Neuhofen" standard soil under aerobic conditions

Column	2	3	4	5	6	7
Day	SN 49 537	Bound residues	Unknown [*]	Origin [*]	¹⁴ CO ₂	Total
0	96.5	3.5	1.6	-	-	101.6
7	74.4	23.3	0.6	1.2	0.1	99.6
14	73.6	26.5	-	-	0.2	100.3
30	71.3	29.8	-	-	0.9	102.0
60	61.9	33.0	0.2	1.4	2.1	98.6
91	55.4	39.2	0.2	1.3	4.9	101.0
182	43.2	38.9	-	1.7	12.2	96.0
360	26.5	43.1	0.3	1.6	27.0	98.5

^{*} Estimated from autoradiographs from TLC-plates
^{**} Calculated in percent of applied dose

Table 3 Results of extraction and combustion of soils from anaerobic studies in % of applied dose

Day	¹⁴ CO ₂	Organic solvent extraction (CH ₃) ₂ CO/CH ₃ OH	H ₂ O- phase	Residues bound to humic and fulvic acids			Combustion	Total	
				{	= fulvic + humic				
30	0.07	46.2	14.7	0.5	21.4	8.2	13.2	18.2	101.1
62	0.03	46.4	7.3	0.1	22.5	8.5	15.6	24.7	101.0
90	0.06	34.0	10.7	0.3	34.1	11.8	21.8	25.9	105.1
120	0.04	36.5	14.4	0.2	22.8	9.1	12.6	23.8	97.7

Table 4 Conversion of SN 49 537 in "Neuhofen" standard soil under anaerobic conditions

Day	SN 49 537	Bound residues	2	Unknown			6	Origin	¹⁴ C O ₂	Total
				3	4	5				
30	29.7	39.6	0.4	3.9	13.1	12.8	1.0	0.6	0.07	101.2
62	35.3	47.2	0.1	5.0	3.9	8.6		1.0	0.03	101.1
90	25.2	60.0	3.5	5.1**	10.3	0.3	0.4	0.06	0.06	104
120	35.5	46.6	5.9**	-	8.9	0.2	0.5	0.04	0.04	97.6

* Percent values calculated in % of applied dose

** A differentiation between both conversion products was not possible

Table 5 Characterization of metabolic products and some standard compounds

1	U n k n o w n				5	6	SN 49 537
	2	3	4				
Rf (1)*	0.58	0	0.12	0.35	0.41	0.45	0.22
Rf (2)*							0.03
Rf (3)*	0.47	0.08	0.09	0.09	0.17	0.20	0.05

* Rf (1), Rf (2), Rf (3) refer to solvent systems

System 1: Ethylacetate

System 2: Benzene/chloroform/acetone = 60 : 30 : 10 (v/v/v)

System 3: Benzene/chloroform/acetone/acetic acid = 60 : 30 : 10 : 4 (v/v/v/v)

Conclusions

- 1) The halflife of SN 49537 in soil under aerobic conditions is about 20 weeks. Bound residues reach 43% of the applied (phenyl labeled) activity at 360 days and 5% of the applied activity is released as $^{14}\text{CO}_2$ at 3 months. Only one degradation product was found but it was not identified and did not exceed 0.6% of the applied after day 7 of incubation.
- 2) Under anerobic conditions (after 30 days of aerobic soil aging), 0.2% of the applied activity is released as $^{14}\text{CO}_2$ indicating microbial degradation to be occurring under only aerobic conditions. There is very little change in the degradation of the parent compound 30 days after establishment of anaerobicity indicating it to be stable under anaerobic conditions. However, additional degradation products do form under anaerobic conditions presumably during the first 30 days after flooding. See table 4 in the results section above.

3.12 Degradation of SN 49537 in an Activated Loamy Sand, Dr. Bruhl, Berlin, January 31, 1980, Acc. No. 070132, Appx. 13, report no R + S 7/80-PA 49 537.71/6

Procedure

A standard German soil (2.2 Neuhofen) that was biologically activated by planting and growing alfalfa in it 4 weeks prior to the study, was fortified with ^{14}C -SN-49537 [N-phenyl-N'-(5- ^{14}C)-thiadiazol-5-yl urea] to a concentration of 2 ppm.

After fortification, the soil was brought to 75% moisture capacity, and stored at 25 °C with a CO_2 trap for 359 days. Samples were taken during incubation and extracted, subjected to TLC and combustion using standard methods.

Soil characteristics are below:

pH	6.6	
organic C	2.36 %	
clay (<2/um)	5.0 %)	
silt (2 - 20/um)	8.3 %)	
fine sand (20 - 200/um)	32.6 %)	100%
coarse sand (0.2 - 2 mm)	54.1 %)	
cation exchange capacity	11.2 mVal/100 g soil	
max. waterholding capacity	36 g H_2O /100 g soil	

Results

Table 2 Extraction of SN 49 537 from a loamy sand

Soil: German standard soll 2.2 ("Neuhofen")

Conditions: aerobic study, biologically activated soil, 75 % max. waterholding capacity
Label: (5-¹⁴C)-thiadiazolyl-SN 49 537
Applied substance: 0.1 mg/sample (\approx 2 mg/kg)
Applied radioactivity: 3.33 x 10⁶ dpm/sample

Values are expressed in % of initially applied product.

Day	¹⁴ CO ₂	Organic solvent extraction		Alkali extraction			Combustion	Total	
		Toluene	Acetone Soxhlet	NaOH = Fulvic + Humic	ac.				
14	1.4	0.4	50.3	15.7	17.5	7.6	9.8	10.0	95.3
72	5.1	0.1	35.2	18.6	20.7	12.9	8.8	16.6	96.3
161	10.0	0.1	28.8	20.8	15.5	8.9	7.0	22.4	97.6
273	13.8	0.1	22.0	20.3	17.1	8.8	9.0	24.8	98.1
359	17.5	0.2	18.4	13.6	18.2	9.9	6.8	28.4	96.3



Breakdown of SN 49 537 in a loamy sand

Soil: German standard soil 2.2 ("Neuhofen")
 Conditions: aerobic study, biologically active soil, 75 % max. waterholding capacity
 Label: (5-¹⁴C)-thiadiazolyl-SN 49 537
 Applied substance: 0.1 mg/sample (\pm 2 mg/kg)
 Applied radioactivity: 3.33 x 10⁶ dpm/sample
 Values are expressed in % of initially applied product.

¹⁴ CO ₂	SN 49 537	Origin	I	II	III	IV	V	VI	Non-extractable residues	Total
1.4	62.6	0.3	0.3	1.1	1.8	0.2	0.1	-	27.5	95.3
5.1	31.6	0.2	0.7	0.2	20.7	0.5	-	-	37.3	96.3
10.0	26.5	0.3	0.4	0.3	21.2	0.7	0.4	-	37.9	97.7
13.8	22.1	0.2	0.4	0.6	17.0	0.8	0.4	0.1	41.9	97.3
17.5	13.7	0.4	-	0.6	14.9	0.8	0.3	-	46.6	94.8
<hr/>										
x 100	42	-	5	15	25	53	64	72	Acetone/diethyl ether, 1 + 1	
	42	-	7	19	29	52	72	90	Ethyl acetate/DNFA, 9 + 1	

Conclusions

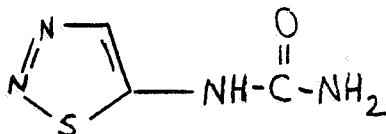
- 1) SN 49537 degraded in the soil with a halflife of about 4 weeks. Only 17.5% of the applied activity was released as $^{14}\text{CO}_2$ during the study indicating little mineralization of the thiadiazole ring over 12 months.
- 2) Six degradation products were detected during the 12 months of soil incubation, but only 1 exceeded 2% of the applied material. None of the degradation products were identified in this study.

3.13 Isolation and Identification of A Conversion Product of Thidiazuron in Soil, Dr. Bruhl, Berlin, August 7, 1980, Acc. No. 070132, Appx. 14.

Appendix to Report R + S 7/80 - PA 49 537.71/6 See section 3.12 above.

Comments

Unknown III, an aerobic soil degradation product, was identified as 1,2,3-thiadiazol-5-yl urea using radio TLC co-chromatography and MS. Its structure is:



3.14 SN 49537 Bare Soil Degradation Study, Test No. Cal 8/76 GR, Acc. No. 070125.

Comments

Only a description of the study without results was submitted. Therefore, field dissipation cannot be assessed at this time from this study.

3.15 Bare Soil Degradation Test with SN 49537, Test No. GA 72/76 GR, Acc. No. 070125.

Comments

Only a description of the study without results was submitted. Therefore, field dissipation cannot be assessed at this time from this study.

3.16 Soil Dissipation of Thidiazuron After Treatment of Cotton with DROPP 50 WP, Acc. No. 070125.

Procedure

A Commerce silt loam soil plot (43.4% sand, 37.0% silt, 19.6% clay, 1.4% OM) was planted to cotton May 10, 1976 and was defoliated on October 14, 1976 by DROPP 50 WP applied at 0.5 lb ai/A. On December 4, 1976, the remaining cotton plant was chopped and disced into the soil. The study was conducted at Friars Pt, MS.

Results

<u>Date of soil sampling</u>	<u>Months after application</u>	<u>Residues in soil (lb ai/A)*</u>	
		<u>0-6"</u>	<u>6-12"</u>
Oct. 14, 1976	0	0.10	<0.10
Jan. 15, 1977	3	0.19	<0.10
Feb. 23, 1977	4	0.19	<0.10

*This is assumed to be equivalent to ppm.

Conclusions

- 1) Decline of residues is not apparent from this study. Persistence has not been ruled out.
- 2) A description of the analytical method was not submitted.

3.17 Soil, Dissipation of Thidiazuron After Treatment of Cotton with DROPP 50 WP, Acc. No. 070125.

Procedure

A sandy clay loam soil plot (1.0-1.5% OM, pH = 7.9 - 8.4) at Alamo, Texas was planted to cotton in Spring 1976 and treated on July 29, 1976 with DROPP 50 WP at 0.5 lb ai/A.

Results

<u>Soil sampling months post-app</u>	<u>Rainfall acc, inches</u>	<u>Residues in soil (lb ai/A)*</u>	
		<u>0-6"</u>	<u>6-12"</u>
0	0	0.10	-
1 1/2	4.12	<0.10	<0.10
7 3/4	23.99	<0.10	<0.10

*assumed to be equivalent to ppm

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Conclusions

Before this study can be evaluated, a description of the analytical method with recovery data is needed.

- 3.18 Soil Dissipation of Thidiazuron After Treatment of Cotton Crop with DROPP 50 WP and Soil Residue Study with SN 49537 (CP 503) on Cotton, Acc. No. 070125.

Procedure

Cotton, growing on Hanford fine sandy loam in Fresno, California was treated when 90% of the bolls were open, with SN 49537 at 0.5 lb ai/A on October 10, 1976. The cotton was machine harvested on October 12, 1976 following by incorporation of the cotton stalks to 6 inches in the soil. Soil samples were taken. The soil profile is 60.5% sand, 32% silt, 8% clay, 0.44% OC, pH = 6.4, CEC = 12.

<u>Months after application</u>	<u>Rainfall acc. inches</u>	<u>Residue in soil 0-6"</u>	<u>(lb ai/A)* 6-12</u>
0	-	0.10	<0.10
2**	0.72	<0.10	<0.10
4	1.91	<0.10	<0.10

* assumed to be equivalent to ppm

**also 6 weeks after incorporation of cotton stubble.

Conclusions

Before this study can be evaluated, description of the analytical method with recovery data is needed.

- 3.19 Soil Dissipation of Thidiazuron After Treatment of Cotton Crop with DROPP 50 WP and Evaluation of SN 49537 Defoliant on Cotton for Residues in Soil, Seed Cotton and Gin Trash, Acc. No. 070125.

Procedure

Cotton was planted in Georgia in a Tifton sandy loam plot (76% sand, 15.6% silt, 8.4% clay, 0.8% OM, 1.6% OM by volume, field moisture = 8.7%, CEC = 5.6, pH = 5.4) and was treated when mature (70% of the bolls open) with SN 49537 one time, at 0.5 lb ai/A Soil samples were taken subsequently.

Climatological data was provided.

Results

<u>Months post application</u>	<u>Residues in soil - (lb ai/A)*</u>		<u>Rainfall (acc. inches)</u>
	<u>0-6*</u>	<u>6-12*</u>	
0	0.16	<0.10	0
1 3/4**	<0.10	<0.10	8.10
3 1/2	<0.10	<0.10	14.08

*assumed to be equivalent to ppm

**about 6 weeks after incorporation of cotton stubble

Conclusions

Before this study can be evaluated, a description of the analytical method with recovery data is needed.

3.20 Rotational Plant Uptake of Thidiazuron Soil Residues, 49537/NA 49, September 18, 1980, Acc. No. 070130.

Procedure

Tifton fine sandy loam plots (soil profile not given) in Cantonment, Florida which were 5' x 20' in size, were treated with SN 49537 50 WP at either 0.25 or 0.5 lb ai/A on September 26, 1977. Barley, bush beans and turnips were planted 23 days after treatment and harvested at various stages of growth. Rotational crops were planted 242 days after treatment and harvested at various stages of growth. It is not known if the plots were plowed before planting. The sampled plants were analyzed for total amounts of thidiazuron and its aniline-containing metabolites using Schering AG residue method 49537/1 dated November 20, 1975.

Climatological data was submitted.

<u>Results</u>	<u>Rate (lb ai/A)</u>	<u>Sampling (days from treatment)</u>	<u>Residue (ppm)</u>
Barley	0.25	71	0.02
Barley	0.5	71	<0.02
Barley	0.25	224	<0.05
Barley	0.5	224	<0.05
Barley	0.25	224	<0.10
Barley	0.5	224	<0.10
Bush beans	0.25	71	<0.03
Bush beans	0.5	71	0.04
Bush beans	0.25	288	<0.03
Bush beans	0.5	288	<0.03
Bush beans	0.25	322	<0.03
Bush beans	0.5	322	<0.03
Turnips	0.25	71	0.07
Turnips	0.5	71	0.05
Turnips	0.25	143	<0.05
Turnips	0.5	143	<0.05
Turnips	0.25	143	<0.02
Turnips	0.5	143	<0.02

Conclusions

- 1) The results of this study indicate the need for a rotational crop restriction such as the following:

"Do not plant small grains or root crops until 1 month after application of DROPP. Only the mature crop may be used for feed or food. Cover crops may be planted but may not be used for feed or food. Other crops may not be planted until 8 months after application.

- 2) This study was not conducted in a manner simulating actual use conditions (DROPP was applied to soil instead of a mature cotton stand). It is conceivable that conducting the study under actual use conditions would have resulted in lower rotational crop residues because the cotton plants would have intercepted the DROPP allowing photolysis to occur and the field would have been plowed causing dilution of the residues in the soil. However, the effect of these factors of dissipation may be negated by a short interval between DROPP application and planting of the rotational crop under actual use conditions.

3.21 Rotational Plant Uptake of Thidiazuron Soil Residues, 49537/NA 63, March 27, 1980, Acc. No. 070130.

Procedure

Cotton fields in Alamo, Texas (soil profile not given) were sprayed with DROPP at 0.25 or 0.50 lb ai/A and the cotton was harvested on August 5, 1976. On September 10, 1976, the field was disced and chiseled, on October 1, 1976 it was bedded and on October 5, 1976 it was planted to cabbage. The cabbage was harvested March 15, 1977.

Soil and cabbage were analyzed using method 49537/1 dated November 20, 1975.

Results

- 1) No detectable residues (<0.02 ppm) were found in the cabbage.
- 2) The soil was sampled at 0, 1/2 and 7 1/2 months post-application to 12" in 6" increments. No detectable residues (<0.10 ppm) were found in the soil after 0 month.

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Conclusion

- 1) No detectable residues will be found in mature cabbage planted 2 months after an application of DROPP to a mature cotton stand

This study supports a 2-month rotational interval for leafy crops.

3.22 Microbial Degradation of Thidiazuron and its Photoproduct, Acc. No. 070131, Appx. 15.

Procedure

In these experiments, thidiazuron and photothidiazuron uniformly labeled in the phenyl moiety were used. Microbiologically active sandy loam soil from the Missouri River bottom and pure microbial cultures were inoculated with the ^{14}C -compounds. The soil was fortified to 38 ppb with thidiazuron or to 107 ppb with photothidiazuron and incubated in the dark for 28 days at 30 °C. The soil was extracted and analyzed using standard radio-analytical techniques.

Pure microbial cultures were grown on 10 ml of yeast-mannitol media for 24 hours and then amended with 10 ul of a $1 \times 10^{-3}\text{M}$ ethanol solution of either ^{14}C -compound. Cultures were incubated, extracted and radioassayed.

Pure cultures of algae were grown on 20 ml of mineral salt culture media under continuous light and aeration for 24 hours before amending the medium with 20 ul of $1 \times 10^{-3}\text{M}$ ethanolic ^{14}C -compound. Cultures were incubated, extracted and radioassayed.

Mass cultures of algae in 400 ml of medium were incubated with 50 ug of cold thidiazuron plus 0.5 u Ci of hot thidiazuron in ethanol. After 24 hours, another 50 ug of cold thidiazuron was added. The culture was incubated with trapping of evolved $^{14}\text{CO}_2$ followed by extraction and radioanalysis.

Results

Table 1. Degradation of thidiazuron-¹⁴C and photothidiazuron-¹⁴C following incubation with soil for

28 days

Soil	% Radioactive material			Relative % ethyl acetate soluble radioactive material		
	Aqueous	Ethyl acetate	Residue	Parent	Phenylurea	Origin
	<u>Thidiazuron</u>					
Non-autoclaved ^a	0.3	48.9	50.8	99.4	0.2	0.4
Autoclaved	0.2	56.7	43.1	98.2	1.0	0.8
<u>Photothidiazuron</u>						
Non-autoclaved	1.0	43.5	55.5	98.3	1.6	0.1
Autoclaved	0.1	61.7	38.2	99.8	0.2	0.0

^a Recovery of thidiazuron from non-autoclaved soil at zero time was 96.6%.

Table 2. Degradation of thidiazuron-¹⁴C by microorganisms following a 42-day incubation^a

% Recovered radioactive material in indicated fraction										
Organism	Aqueous	Ethyl acetate ^b								
		I	II	III	IV	V	VI	VII	VIII	IX X
		(0.76)	(0.68)	(0.51)	(0.49)	(0.39)	(0.27)	(0.16)	(0.11)	(0.07) (0.00)
<u>Aerobacter aerogenes</u>	7.4	0.1	0.4	0.5	0.6	89.8	0.6	0.2	<0.1	0.1 0.3
<u>Aeromonas liquefaciens</u>	5.1	0.1	0.5	0.3	2.4	89.0	1.2	0.3	<0.1	0.2 0.9
<u>Bacillus cereus</u>	6.2	0.2	0.5	0.2	2.9	86.1	2.5	0.5	<0.1	0.3 0.6
<u>Bacillus megaterium</u>	11.3	0.1	0.4	0.5	1.8	83.9	0.8	0.4	<0.1	0.4 0.4
<u>Bacillus subtilis</u>	3.6	0.1	0.5	0.8	2.9	90.5	0.8	0.2	<0.1	0.4 0.2
<u>Flavobacter sp.</u>	16.3	0.3	0.4	0.3	0.5	78.4	2.3	0.3	<0.1	0.6 0.6
<u>Proteus vulgaris</u>	12.2	0.1	0.4	2.2	0.2	83.1	0.9	0.2	<0.1	0.3 0.4
<u>Pseudomonas putida</u>	11.6	0.1	0.4	1.1	1.0	82.6	1.9	0.3	<0.1	0.5 0.5
<u>Aspergillus versicolor</u>	21.0	0.2	1.2	0.3	2.2	70.6	3.0	0.2	<0.1	0.4 0.9

Table 2. (Continued)

% Recovered radioactive material in indicated fraction										
Organism	Aqueous	Ethyl acetate ^b								
		I	II	III	IV	V	VI	VII	VIII	IX X
		(0.76)	(0.68)	(0.51)	(0.49)	(0.39)	(0.27)	(0.16)	(0.11)	(0.07) (0.00)
<u>Penicillium cyclopium</u>	3.0	0.1	0.4	0.5	1.0	92.5	0.8	0.3	<0.1	0.9 0.5
<u>Torula rosea</u>	22.3	0.1	0.3	0.3	0.6	74.5	0.9	0.2	<0.1	0.5 0.3
Control	1.9	0.1	0.4	0.5	1.3	92.9	0.8	0.3	<0.1	1.3 0.5

^a Samples also analyzed at 14, 21, and 28 days; only data obtained from the 42-day incubation are shown here to conserve space.

^b Components of ethyl acetate fraction separated by TLC on silica gel GF₂₅₄; solvent system was ethyl acetate. Compound II cochromatographed with photothidiazuron; Compound V cochromatographed with thidiazuron; Compound VI cochromatographed with phenylurea; and Compound VIII cochromatographed with 4-hydroxyphenylurea; other compounds are unknown. R_f values given in parentheses.

Table 3 - Degradation of photothidiazuron - ^{14}C by microbes following a 28 day incubation
% Recovered radioactive material in indicated fraction

Organism	Aqueous	Ethyl acetate ^a								
		I	II	III	IV	V	VI	VII	VIII	IX
		(0.63)	(0.55)	(0.50)	(0.41)	(0.39)	(0.27)	(0.10)	(0.04)	(0.00)
<u>Aerobacter aerogenes</u>	4.4	94.4	<0.1	0.4	0.4	<0.1	0.1	<0.1	0.1	0.2
<u>Aeromonas liquefaciens</u>	3.4	95.6	<0.1	0.4	<0.1	<0.1	0.2	<0.1	0.2	0.2
<u>Bacillus cereus</u>	3.6	92.9	<0.1	0.7	1.2	<0.1	0.8	<0.1	0.3	0.6
<u>Bacillus megaterium</u>	9.0	81.8	2.3	2.7	1.0	0.3	0.7	<0.1	0.6	1.5
<u>Bacillus subtilis</u>	10.9	80.2	4.9	<0.1	0.4	0.8	1.5	<0.1	0.4	0.9
<u>Flavobacter sp.</u>	6.3	91.2	<0.1	0.3	0.2	0.1	0.5	<0.1	0.4	1.0
<u>Proteus vulgaris</u>	5.1	93.4	<0.1	0.5	0.2	0.1	0.3	<0.1	0.2	0.2
<u>Pseudomonas putida</u>	9.1	87.9	<0.1	0.6	0.5	0.3	0.5	<0.1	0.3	0.9
<u>Aspergillus versicolor</u>	44.0	21.3	28.8	0.8	0.8	0.4	1.5	0.8	0.5	1.1
<u>Penicillium cyclopium</u>	45.5	28.9	3.1	9.2	0.9	1.1	7.5	0.9	0.7	2.2
<u>Torula rosea</u>	10.7	83.0	<0.1	0.4	4.1	0.1	1.3	<0.1	0.3	0.1
Control	2.4	95.1	<0.1	<0.1	0.6	<0.1	<0.1	0.2	0.3	1.4

^a Components of ethyl acetate fraction separated by TLC on silica gel GF₂₅₄; solvent system was ethyl acetate.

Compound I cochromatographed with photothidiazuron; Compound II cochromatographed with 4-hydroxyphenylphotothidiazuron; Compound V cochromatographed with thidiazuron; Compound VI cochromatographed with phenylurea; and Compound VII cochromatographed with 4-hydroxyphenylurea; other compounds are unknown. R_f values given

Table 4. Degradation of thidiazuron-¹⁴C by algae

		% Recovered radioactive material in indicated fraction				
		Ethyl acetate ^a				
Incubation		II	V	VI	IX	X
time, days	Aqueous	(0.68)	(0.39)	(0.27)	(0.07)	(0.00)
<u>Chlorella sp.</u>						
3	26.8	59.8	7.0	2.0	3.1	1.3
7	38.5	44.8	2.0	11.6	2.0	1.1
14	48.1	29.5	1.6	18.0	1.6	1.2
<u>Oscillatoria sp.</u>						
3	31.7	54.5	9.4	3.0	0.4	1.0
7	42.6	44.0	2.1	9.0	0.9	1.4
14	50.5	30.3	2.1	14.5	0.7	1.9
<u>Control</u>						
7	21.1	64.3	4.9	3.5	<0.1	6.2
14	37.5	52.8	2.1	1.9	<0.1	5.7

^a Components of ethyl acetate fraction separated by TLC on silica gel GF₂₅₄; solvent system was ethyl acetate. Compound II cochromatographed with photothidiazuron; Compound V cochromatographed with thidiazuron; and Compound VI cochromatographed with phenylurea. R_f values given in parentheses.

Table 5. Degradation of photothidiazuron- ^{14}C by algae

		% Recovered radioactive material in indicated fraction							
		Ethyl acetate ^a							
Incubation		I	II	III	IV	VI	VII	VIII	IX
time, days	Aqueous	(0.63)	(0.55)	(0.50)	(0.41)	(0.27)	(0.10)	(0.04)	(0.00)
<u>Chlorella sp.</u>									
3	14.5	82.3	0.8	1.4	0.1	0.4	0.2	<0.1	0.3
7	22.1	72.2	1.6	1.2	0.2	1.9	0.2	<0.1	0.6
14	38.3	45.5	0.9	7.2	1.4	3.7	0.7	0.2	2.1
<u>Oscillatoria sp.</u>									
3	15.8	75.5	1.6	4.5	0.7	0.6	0.1	0.1	1.1
7	26.3	61.9	1.3	5.5	0.9	1.8	0.3	0.3	1.7
14	36.1	51.5	1.2	1.8	0.4	7.7	0.4	0.3	0.6
<u>Control</u>									
7	13.5	73.4	2.2	6.0	1.0	0.3	0.3	0.3	3.0
14	24.3	67.4	2.6	1.4	1.3	0.6	1.1	0.2	1.1

^a Components of ethyl acetate fraction separated by TLC on silica gel GF₂₅₄; solvent system was ethyl acetate. Compound I cochromatographed with photothidiazuron; Compound II cochromatographed with 4-hydroxyphenylphotothidiazuron; Compound VI chchromatographed with phenylurea; and Compound VII cochromatographed with 4-hydroxyphenylurea. R_f values given in parentheses.

Conclusions

- 1) It was shown that microbes can degrade thidiazuron to at least 9 different products.
- 2) No product exceeded 3% of the applied during 42 days of incubation and greater than 70% of the parent compound remained.
- 3) This study also showed photothidiazuron to be subject to microbial metabolism but no new products formed other than those that result from thidiazuron microbial metabolism.
- 4) It was not stated whether the microbes used in this study are soil microbes common to the proposed use area.

3.23 The Influence of DROPP on Selected Microbiological Processes in Soils, Acc. No. 070131, Appx 16.

Procedure

The effects of DROPP on microbiological processes in soils were studied. The soils, (presumably of European origin) were a parabrown soil (1.26% OC, pH = 5.4), a chernosem (2.3% OC, pH = 7.5) and an organic compost (13.59% OC, pH = 7.2) and were sieved at 2 mm.

The soils were fortified to 2 or 20 ppm (dry weight) with DROPP and were incubated in the dark at 22 °C. To study nitrogen fixation, however, incubation was at 30 °C and presumably not in the dark.

Results/Conclusions

DROPP, at 2 or 20 ppm in the soil, had no significant impact on nitrogen fixation under anaerobic or aerobic conditions, on ammonification, on nitrification, on fungal colonization of soil particles, or on the numbers of bacteria, actinomycetes and fungi.

3.24 Leaching of SN 49537 in Soil Columns, 49537/NA 14, May 14, 1976, Acc. No. 070131, Appx. 17.

Procedure

PVC columns (4" i.d.) were filled to 12 inches with soil. Four different soils were used and are described below

Soil Characteristics of Leaching Column Soils

Soil Characteristics	Soil Types			
	Florida Sand	Miami Silty Loam	Drummer silty Clay Loam	Summer Sandy Loam
pH range	6.8-7.0	7.4-7.6	7.8-8.0	7.4-7.6
organic content	1.1%	1.8%	5.7%	2.4%
Moisture Content (as received)	9%	16%	20%	17%
% Coarse Sand	38%	16%	15%	40.5%
% Fine Sand	53.5%	32%	15%	28%
% Silt	3%	32%	30.5%	12%
% Clay	2%	13%	27%	8.5%
Loss on Ignition	-	7%	10%	8%

The soil surface was treated at an equivalent rate of 0.5 lb ai/A and the column was then leached with an equivalent of 6 acre inches per day for 5 days.

Table 1 Characteristics of the Soils Tested (refer to section 3.2.5)

	Standard soil 2.2, "Neuhofen" (a)	Standard soil 2.3, "Hatzenbühl" (a)	Sandy soil (b)
pH	5.7	5.0	7.0
Organic C (%)	1.93	0.99	6.60
Clay, <2 _μ m (%)	7.3	5.9	2.7)
Silt, 2-20 _μ m (%)	6.5	14.1	3.1)
Fine sand, 20-200 _μ m (%)	29.0	39.3	64.2)
Coarse sand, 0.2-2 mm (%)	57.2	40.7	30.0)
Max. waterholding capacity, g H ₂ O/100 g soil	30	30	57 (c)
Soil type (d)	loamy sand	loamy sand	sand

Soil analyses: (a) Landwirtschaftliche Untersuchungs- und Forschungsanstalt, Speyer am Rhein.
January 1, 1978

(b) Landwirtschaftliche Untersuchungs- und Forschungsanstalt, Speyer am Rhein,
June 8, 1978

(c) Carried out in our laboratories based on a method described in "Bodenkundliches Praktikum", E. Schlichting, H.-P. Blume, Verlag Paul Parey, Berlin 1966, p. 67.

(d) Soil Taxonomy, Agriculture Handbook No. 436, U.S. Department of Agriculture,
December 1975, p. 470-471

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Results

No detectable residues (<0.02 ppm) were found in the percolation water in any experiment.

Conclusions

Leaching of thidiazuron will not occur.

- 3.25 Mobility of Phenyl- ^{14}C -Thidiazuron in Three Soils, Dr. Bruhl, Berlin, November 6, 1980, Acc. No. 070131, Appx. 17 a.

Procedure

Segmented glass, cylinder columns (30 cm x 5 cm i.d.) were filled with German standard soils (described below) and were prewetted. The top of the columns were then treated with 30 ug ai and were then leached with 10 cm deionized water per day for 6 days in a continuous manner.

Results

- 1) About 95% of the recovered activity was found in the top 6 cm of soil.
- 2) Less than 2% of the applied material was found in the eluate.

Conclusions

Leaching of thidiazuron will not occur.

- 3.26 Mobility of Carbonyl- ^{14}C -Thidiazuron in Four Soils, Dr. Bruhl, Berlin, October 27, 1980, Acc. No. 070131, Appx. 17 c.

Procedure

Segmented glass columns were filled with the soils described in the study below (section 3.27) and were prewetted. The tops of the columns were then treated with 50 ug of ai and leached with 10 cm of deionized water per day for 6 days in a continuous manner.

Results

- 1) In all cases 94-97% of the applied ^{14}C was found in the top 5 cm.
- 2) Less than 2% of the applied ^{14}C was found in the eluate.

Conclusions

Leaching of thidiazuron will not occur.

- 3.27 Mobility of 5 - ^{14}C -Thiadiazolyl-Thidiazuron in Four Soils, Dr. Bruhl, Berlin, October 31, 1980, Acc. No. 070131, Appx. 17b.

Procedure

Segmented glass columns were filled with the soils described below and were prewetted. The tops of the columns were then treated with 50 ug ai and leached with 10 cm deionized water per day for 6 days in a continuous manner.

Results

- 1) In all cases, 96-99% of the applied activity was found in the top 6 cm.
- 2) Less than 3% of the applied material was found in the eluate.

Conclusions

Leaching of thidiazuron will not occur.

- 3.28 Leaching of SN 49537, Dr. Bruhl, Berlin, May 17, 1976, Acc. No. 070131, Appx. 18.

Table 1 Characteristics of the Soils Tested (refer to section 3.27)

	Standard soil 2.2, "Neuhofen" (a)	Standard soil 2.3, "Hatzenbühl" (a)	Sandy soil (b)	Sandy loam (c)
pH	5.7	5.0	7.0	5.9
Organic C (%)	1.93	0.99	6.60	1.03
Clay, <2 _{um} (%)	7.3	5.9	2.7	15.6)
Silt, 2 - 20 _{um} (%)	6.5	14.1	3.1	14.1)
Fine sand, 20 - 200 _{um} (%)	29.0	39.3	64.2	42.1)
Coarse sand, 0.2 - 2 mm (%)	57.2	40.7	30.0	28.2)
Max. waterholding capacity, g H ₂ O/100 g soil	30	30	57 (d)	-
Soil type (e)	loamy sand	loamy sand	sand	sandy loam

- Soil analyses:
- (a) Landwirtschaftliche Untersuchungs- und Forschungsanstalt, Speyer am Rhein, January 1, 1978
 - (b) Landwirtschaftliche Untersuchungs- und Forschungsanstalt, Speyer am Rhein, June 8, 1978
 - (c) Landwirtschaftliche Untersuchungs- und Forschungsanstalt, Speyer am Rhein, February 6, 1979
 - (d) Carried out in our laboratories based on a method described in "Bodenkundliches Praktikum", E. Schlichting, H.-P. Blume, Verlag Paul Parey, Berlin, 1966, p. 67.
 - (e) Soil Taxonomy, Agriculture Handbook No. 436, U.S. Department of Agriculture, December 1975, p. 470-471

Procedure

Three leaching experiments were conducted using ^{14}C -SN 49537 [N-phenyl-N'-([5- ^{14}C]-1, 2, 3-thiadiazole-5-yl)-urea] and German standard soil 2.2.

Expt 1 - A dry soil column was overlaid with 4 gm of ^{14}C -DROPP fortified soil.

Expt 2 - A prewetted soil column was overlaid with the fortified soil.

Expt 3 - A prewetted column was overlaid with fortified soil that was aged for 40 days prior to overlaying.

Results

- 1) Experiment 1 was discontinued because water percolated through the column even though the column was not thoroughly wet.
- 2) Greater than 95% of the recovered activity remained in the top 5 cm of the columns and 2% or less of the applied activity was found in the eluate of experiments 2 and 3.

Conclusions

- 1) Parent thidiazuron or soil aged thidiazuron residues will not leach.

3.29 Mobility of SN 49537 After Aging in a Loamy Sand, Dr. Bruhl, Berlin, November 30, 1978, Acc. No. 070131, Appx. 19.

Procedure

^{14}C -Phenyl labeled SN 49537 (32.4 ug) was added to 50 gm of German standard soil 2.2 (Neuhofen) and aged for 30 days at 24 °C in the dark. A sample of the aged soil was placed on top of untreated soil on a column (30 cm x 5 cm i.d.) and irrigated with 0.5 inch of deionized water per day for 45 days. Soil profile was provided.

Results

- 1) From 93-106% of the applied ^{14}C was found in the top 5 cm of the columns. Less than 1% of the applied ^{14}C was found in the leachate.

Conclusions

Soil aged thidiazuron residues will not leach.

- 3.30 Adsorption - Desorption of Thidiazuron in Soil and Sediment,
Dr. Bruhl, Berlin, December 21, 1979, Acc. No. 070131,
Appx. 20.

Procedure

German standard soil 2.2 (Neuhofen) and sediment from the Havel River in northern Berlin were used are described below.

	<u>2.2 Neuhofen</u>	<u>Sediment</u>
pH	5.6	6.6
organic C	2.19	0.33
clay	8.8	0.2
silt	6.4	0.8
sand	84.8	99.0

^{14}C -Thidiazuron labeled in the phenyl moiety was used.

Soil samples (1.6 grams) were shaken with aqueous solutions of 14 -thidiazuron of the following appx. concentrations: 0.1, 1, 5, 10 and 20 ppm. Shaking was done for 24 hours at 20 °C, was followed by centrifuging and sampling the supernatant for radioanalysis. Desorption was then carried out using 0.01 M $\text{Ca}(\text{N})_3)_2$ a total of 5 times.

Results

Table 1 Adsorption-Desorption of Thidiazuron in "Neuhofen" Soil

Soil type: "Neuhofen", German standard soil 2.2 (cf. Table 1)
 Soil/sample: 1.6 g Volume of pesticide solution: 8 ml
 All values in $\mu\text{g/g}$ with respect to solutions or soil.

Temperature: 20 °C

Initial concentration Sample	17		8.5		4.3		0.89		0.08	
	1	2	3	4	5	6	7	8	9	10
<u>Adsorption</u> solution										
Equ. Conc. soil	3.56	4.61	1.79	1.71	0.898	0.896	0.0871	0.0896	0.00424	0.00475
	66.8	61.9	33.1	32.6	16.7	16.9	3.89	3.88	0.387	0.385
<u>1. Desorption</u> solution										
Equ. Conc. soil	2.22	2.11	0.875	0.882	0.434	0.406	0.0569	0.0582	0.00320	0.00295
	58.2	54.2	29.9	29.5	15.1	15.4	3.67	3.65	0.374	0.374
<u>2. Desorption</u> solution										
Equ. Conc. soil	1.63	1.51	0.679	0.711	0.301	0.299	0.0429	0.0437	0.00319	0.00247
	51.5	48.0	27.2	26.7	13.9	14.2	3.49	3.47	0.361	0.363
<u>3. Desorption</u> solution										
Equ. Conc. soil	1.39	1.20	0.560	0.573	0.229	0.251	0.0387	0.0404	0.00226	0.00215
	45.7	43.0	24.9	24.4	13.0	13.1	3.33	3.30	0.352	0.354
<u>4. Desorption</u> solution										
Equ. Conc. soil	0.977	0.932	0.449	0.454	0.188	0.225		0.0352	0.00204	0.00191
	41.8	39.1	23.0	22.5	12.2	12.2		3.15	0.343	0.346
<u>5. Desorption</u> solution										
Equ. Conc. soil	0.812	0.777	0.376	0.388	0.187	0.180		0.0313	0.00174	
	38.4	35.8	21.4	20.9	11.4	11.4		3.02	0.336	

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Table 2 Adsorption-Desorption of Thidiazuron

Soil type: Sediment (cf. Table 1)

Soil/sample: 1.6 g Volume of pesticide solution: 8 ml

Temperature: 20 °C

All values in [$\mu\text{g/g}$] with respect to solutions or soil.

Initial concentration Sample	18		9	4.5		0.9			0.1
	1	2		4	5	6	7	8	
<u>Adsorption</u> Equ. Conc. solution soil	13.7	13.85	6.73	3.28	2.37	0.621	0.622	0.0573	0.0191
	20.3	19.8	11.4	6.19	6.15	1.49	1.51	0.191	0.162
<u>1. Desorption</u> Equ. Conc. solution soil	3.16	3.18	1.55	0.787	0.830	0.162	0.169	0.0172	0.0168
	12.1	12.3	7.35	4.10	3.93	1.02	1.02	0.140	0.111
<u>2. Desorption</u> Equ. Conc. solution soil	1.00	0.935	0.471	0.260	0.257	0.0581	0.0581	0.00704	0.00641
	9.90	9.47	5.83	3.21	3.11	0.818	0.826	0.115	0.0882
<u>3. Desorption</u> Equ. Conc. solution soil	0.429	0.393	0.223	0.123	0.128	0.0282	0.0318	0.00387	0.00361
	8.38	8.04	5.01	2.75	2.63	0.716	0.703	0.101	0.0742
<u>4. Desorption</u> Equ. Conc. solution soil	0.180	0.187	0.0986	0.0578	0.0615	0.0127	0.0185	0.00230	0.00240
	7.73	7.34	4.64	2.52	2.40	0.670	0.631	0.0914	0.0646
<u>5. Desorption</u> Equ. Conc. solution soil	0.0974	0.0912	0.0511	0.0312	0.0322	0.00864	0.00936	0.00157	0.00137
	7.36	7.00	4.44	2.39	2.27	0.635	0.595	0.0850	0.0592

Table 3

Freundlich Equation Parameters for Adsorption of Thidiazuron

Soil type	"Neuhofen" 2.2	Sediment
K	21.3	2.22
1/N	0.74	0.87
Range of validity [$\mu\text{g/g}$ solution]	0.004 - 3	0.06 - 13
Correlation coefficient	1.00	1.00

Calculation of the parameters was carried out using all adsorption data from Tables 2 and 3, respectively.

Table 4 Freundlich Equation Parameters for Desorption of Thidiazuron

Soil type

"Neuhofen" 2.2

Initial concentration
of adsorbed thidiazu-
ron [$\mu\text{g/g}$]

17	8.5	4.3	0.9	0.8
Sample No. (Table 2)				
1	3	5	8	9
K	41.8	29.3	17.6	6.99
1/N	0.38	0.28	0.22	0.15
Correlation coefficient	0.99	0.94	0.93	0.95

Sediment

Initial concentration
of adsorbed thidiazu-
ron [$\mu\text{g/g}$]

18	9	4.5	0.9	0.1
Sample No. (Table 3)				
1	3	4	7	8
K	10.6	7.19	4.50	1.59
1/N	0.20	0.19	0.21	0.23
Correlation coefficient	0.94	0.95	0.97	1.00

ff

Conclusions

The Freundlich K value of 21.3 for the Neuhofen soil indicates moderately strong soil binding and would indicate little leaching to occur. Even after 5 desorption runs, the soil equilibrium concentration decreased at most by less than half (43%). Desorption decreased with decreasing soil concentration.

3.31 Thidiazuron Uptake, Distribution and Metabolism in Bluegills and Channel Catfish, Knowles, C.O. et al, Acc. No. 070131, Appx. 21.

Procedure

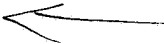
Two bluegill flow-through and 2 catfish static accumulation studies were run using 2 different ^{14}C -radiosamples of thidiazuron, one labeled uniformly in the phenyl moiety and one labeled at the thiadiazole carbon adjacent to the urea nitrogen.

The flow-through studies resulted in a concentration of 0.1 ppm ai and a maximum of 50 uL/L water of DMF (the carrier solvent). The temperature was kept $22 \pm 1^\circ\text{C}$.

In the static study, the ^{14}C material was added to a sandy loam resulting in a concentration 0.15 ppm. The soil was aged aerobically for 14 days and then flooded slowly with well water. Catfish were then added.

The remaining aspects of these experiments were run according to standard methods.

Results

- 1) Bioconcentration factors in bluegill fillet (upper) and offal (lower) tissues exposed to phenyl-labeled thidiazuron did not exceed 8 X but reached 54 X when exposed to the thidiazuron labeled at the thiadiazole carbon adjacent to the urea nitrogen. After 28 days of exposure, these maximum levels dropped by 2/3 (to 1/3 of the maximum). 
- 2) Bioconcentration factors in catfish fillet and offal tissues did not exceed 1X. In the catfish study, ^{14}C -thidiazuron levels in the water did not exceed 1 ppb.

Conclusions

- 1) Thidiazuron will not accumulate in fish.
- 2) Residues found in fish were at levels too low for identification.

4. Conclusions

Thidiazuron is stable to hydrolysis but will photodegrade in aqueous solution and on soil surfaces to an isomer of the parent which is known as photoproduct #2 or photothidiazuron.

Thidiazuron degrades in soil with a halflife, under aerobic conditions, of 4-20 weeks depending on which moiety is being monitored. Refer to sections 3.11 and 3.12. Under field conditions, thidiazuron was not found to persist but a description of the analytical method is needed.

The rotational crop studies, which were not conducted under use conditions, support the following restriction: "Do not plant small grains or root crops until 1 month after application of DROPP. Do not plant leafy crops until 2 months after application of DROPP. Only the mature small grain, root crop and leafy crop may be used for food or feed. Cover crops may be planted after cotton harvest but may not be used for food or feed. Other crops may not be planted until 8 months after application".

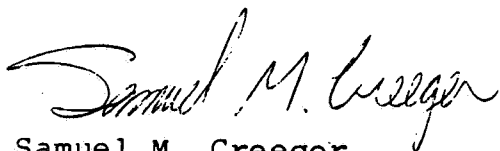
Microbial processes in the soil will not be affected by use rates of thidiazuron. Also, microbes can degrade thidiazuron, but it is not known if the microbes used in the study were soil microbes common to the proposed use area.

Thidiazuron or soil aged thidiazuron residues will not leach and will not accumulate in fish.

5. RECOMMENDATIONS

- 5.1 We concur with the proposed use of thidiazuron as a cotton defoliant if the following will be addressed:
 - 5.1.1 Submit a description of the analytical method used with recovery data for the following field dissipation studies:
 - Soil Dissipation of Thidiazuron After Treatment of Cotton with DROPP 50 WP (2 studies - Friars Point, MS, and Alamo, TX).

- ° Soil Residue Study with SN 49537 (CP 503) on Cotton.
 - ° Evaluation of SN 49537 Defoliant on Cotton for Residue in Soil, Seed Cotton and Gin Trash.
- 5.1.2 The following or similar rotational restriction be placed on the label:
- "Do not plant small grains or root crops until 1 month after application of DROPP. Do not plant leafy crops until 2 months after application of DROPP. Only the mature small grain, root crop and leafy crop may be used for food or feed. Cover crops may be planted after cotton harvest but may not be used for food or feed. Other crops may not be planted until 8 months after application."
- 5.1.3 Provide information on whether the microbes used in the study on "Microbial Degradation of Thidiazuron and its Photoproduct" are soil microbes common to the proposed use areas.
- 5.1.4 Are the soil residues found in the field dissipation studies listed in 5.1.1 above and reported in units of lb ai/A equivalent to units of ppm?
- 5.1.5 Regarding "Rotational Plant Uptake of Thidiazuron Soil Residues, 49537/NA 49," were the treated plots plowed before planting of rotational crops?



Samuel M. Creeger
October 9, 1981
Review Section #1/EFB
Hazard Evaluation Division