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DATE: February 26, 1979

To: Product Manager Wilson (21)
TS-767

Through: Dr. Gunter Zweig, Chief
Environmental Fate Branch

From: Review Section No. 1
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 100-ANN

Chemical: N-(2,6-dimethylphenyl)-N-(methoxyacetyl)alanine methyl ester (Ridomil)

Type Product: Fungicide

Product Name: CGA-48988 5W Fungicide

Company Name: CIBA-GEIGY

Submission Purpose: use on non-bearing citrus (FA.) and ornamentals

Date in: 9/28/78

Date out: 2/26/79

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1. INTRODUCTION

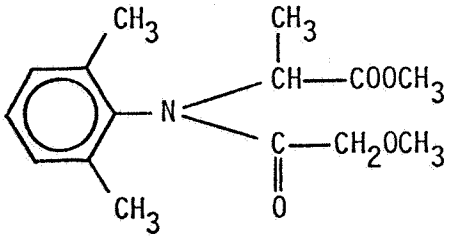
1.1 The fungicide CGA-48988 (Ridomil) in a 5W formulation is being proposed for registration on ornamentals and non-bearing citrus (Florida).

1.2 Other reviews are:

100-EUP-1, potatoes, Nov. 1, 1978
100-EUP-62, tobacco, (in final typing)
100-ANR, for manufacturing use (being reviewed concurrently)

1.3 The accession number of this submission is 235065 and all supporting environmental fate data has been referenced in accession numbers 234438 annd 234431 (both volumes submitted with 100-EUP-62).

1.4 Structure of CGA-48988



2. DIRECTIONS FOR USE

2.1 Plant	Soil Drench	Soil Mix	Foliar Spray
Foliage	0.1-0.5 oz ai/400-800 ft^2 at 2-3 mo. intervals	0.025-0.1 oz ai/yd^3	
Bedding, at seeding. at transplanting	0.063-0.125 oz ai/800 ft^2 0.125-0.5 oz ai/800 ft^2 at 1-2 mo. intervals	0.025-0.05 oz ai/yd^3 0.025-0.05 oz ai/yd^3	
Flowers	0.125-0.5 oz ai/400-800 ft^2 at 1-2 mo. intervals		
Azaleas	0.25-0.60 oz ai/400-800 ft^2 at 2-4 mo. intervals		0.30-0.60 oz ai/100 gal., spray to run-off, repeat at 2-3 mo. intervals do not exceed 1 oz ai/6 mo.
Woody ornamentals	0.25-1.0 oz ai/400-800 ft^2 at 2-3 mo. intervals		
Non-bearing citrus* in citrus nurseries (Fla. only)	1.0-3.75 oz ai/1000 ft row in a 2 foot band at 3-5 mo. intervals		

* Non-bearing citrus seedlings or trees in nurseries that will not bear fruit within 12 months after application.

2.2 Do not contaminate water, food, or feed by storage, disposal, or cleaning of equipment. Open dumping is prohibited. Pesticide, spray mixture, or rinsate that cannot be used or chemically reprocessed should be disposed of in a landfill approved for pesticides or buried in a safe place away from water supplies. Dispose of in an incinerator or landfill approved for pesticide containers, or bury in a safe place. Consult federal, state, or local disposal authorities for approved alternative procedures such as limited open burning.

2.3 Keep out of lakes, streams, or ponds. Apply only as specified on this label. Do not apply when weather conditions favor drift from treated areas. Do not contaminate water by cleaning of equipment or disposal of wastes.

3. DISCUSSION OF DATA

3.1 Gas Chromatographic Method for the Determination of Residues of CGA-48988 and its Acid Metabolite CGA-62826 in Soil, method no. AG-323

Soil treated with Ridomil is extracted with 50% aqueous methanol which is then made basic with NaOH. The parent is removed from this by extraction with dichloromethane which is then cleaned up and subjected to GC analysis with a flame ionization detector. Residues of the acidic metabolite CGA-62826 [N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl) alanine] are removed from the basified solution by acidification with HCl and partitioning with dichloromethane which is evaporated to dryness and reacted with diazomethane which converts the CGA-62826 via methylation to parent CGA-48988 which is cleaned up and detected as unchanged parent, above.

Section 3.2 below shows this method to be acceptable.

3.2 Validation of Analytical Method AG-323 for the Determination of Residues of CGA-48988 and its Acid Metabolite CGA-62826 in Soil, report # ABR-78048 acc. #234438, pg 32-38.

Soil treated with Ridomil is extracted with 50% aqueous methanol which is then made basic with NaOH. The parent is removed from this by extraction with dichloromethane which is then cleaned up and subjected to GC analysis with a flame ionization detector. Residues of the acidic metabolite CGA-62826 [N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl) alanine] are removed from the basified solution by acidification with HCl and partitioning with dichloromethane which is evaporated to dryness and reacted with diazomethane which converts the CGA-62826 via methylation to parent CGA-48988 which is cleaned up and detected as unchanged parent, above.

Validation studies were run using soils fortified with CGA-48988 and CGA-62826 from 0.05 to 10.0 ppm and a soil treated with CGA-48988 at 0.25 lb ai/A and aged for 12 weeks in the greenhouse. (See 3.12 ~~above~~ below for experimental conditions).

Results

1) % recoveries of CGA-48988 and CGA-62826 from soils fortified in the range of 0.05 - 10.0 ppm averaged 97 ± 14 and 104 ± 11, respectively.

2) With regard to determining parent and CGA-62826 in the solvent after soil extraction from aged soils, this method (AG-323) is comparable to LSC.

Conclusions

1) Method AG-323 is acceptable.

3.3 Hydrolysis of CGA-48988 under Laboratory Conditions, project report 26/76, Basle, August 10, 1976, pages 39-56.

The hydrolysis of buffered solutions of CGA-48988 at 100 ppm were monitored at various pH's and temperatures. Analysis was accomplished by extraction of an aliquot of the buffered solution with methylene chloride followed by evaporation and taking up the residue with acetone. CGA-48988 in the acetone was determined by GC with a PN detector.

Studies using ^{14}C ring labeled CGA-48988 in 0.1N HCl and in pH 10 buffer at 70°C were run to identify degradation products. GC - MS techniques were used.

Recoveries were 95-100%.

Conclusions

1) At pH 5, 7 and 9 and at 20-30°C, the halflife of CGA-48988 is not reached before 4 weeks.

2) At pH 9-10 at 50-70°C, the halflife varies from 5 hours to 5 days. The halflife of the parent is 12 days in 0.1 N HCl at 70°C.

3) CGA-48988 is stable to the hydrolytic conditions normally found in the environment.

4) Under prolonged or exaggerated conditions (see results) when significant hydrolysis does occur, only one degradation product is found. It is N-2, 6-dimethylphenyl-N-(2'-methoxyacetyl) alanine.

3.4 Photolysis of CGA-48988 (Ridomil) on Soil Surfaces under Artificial Sunlight Conditions, project report 09/78, Basle, Switzerland, Feb. 14, 1978.

An oven dry silty loam from Switzerland (38.4% sand, 49.4% silt, 12.2 % clay, 3.6% OM, pH= 6.1 and moisture capacity = 38%) was fortified with ^{14}C - labeled CGA-48988 to 10 ppm and half of the samples were then moistened to 12%. Six metal boxes, each with a surface area of 88 cm^2 were filled to 0.6-0.7 cm deep with the fortified soil. The soil was then exposed to xenon arc radiation with IR and UV filters thereby simulating the natural sunlight spectrum but was of approximately twice the intensity (940 ± 50 J x m^{-2} x s^{-1}). Exposure lasted for 24 and 72 hours and the sample temperature remained at 45 ± 5°C.

After exposure, the soil was Soxhlet extracted first with acetone and then methanol. The extracts were analyzed by GC with a PN - detector.

Covered samples were also run as controls.

Results

1) There was no difference between the covered and exposed samples with regard to ^{14}C analysis and GLC analysis of the extracts.

Conclusions

1) CGA-48988 on soil surfaces is stable to photolysis.

3.5 Degradation of CGA-48988 (Ridomil) in Soil Under Aerobic, Aerobic/Anaerobic and Sterile/Aerobic Conditions, project report 08/78, Basle, Feb. 14, 1978.

Dry aliquots of clay loam soil in which potatoes had been growing the previous 9 weeks and of the following characteristics (83.8% sand, 7.3% silt, 8.9% clay, 2.2% OM, CEC = 11.3 meq/100 gm soil, pH = 6.5, water capacity = 34.0 gm water/100 gm soil) were fortified with ^{14}C ring labeled CGA-48988 to 10 ppm.

The fate of the CGA-48988 was monitored under the following conditions:

aerobic incubation - The soil was brought to and maintained at 75% moisture capacity and ventilated with air at 60 ml/min. in the dark at 25°C. The soil and gas traps containing ethylene glycol monomethyl ether, NaOH and H_2SO_4 were analyzed.

aerobic/anaerobic incubation - Soil, aerobically aged for 30 days, was covered with 2-3 cm distilled water, ventilated with N_2 four times a day for 15 minutes at 60 ml/min and incubated at 25°C.

Sterile/aerobic incubation - The soil was sterilized by autoclaving, then fortified with the ^{14}C-ai and moistened to 75% of capacity with distilled water. Incubation was in the dark at 25°C and sterile conditions were maintained.

The soil was analyzed as described in the study titled "Distribution and Degradation of CGA-48988 (Ridomil) in a Field Soil" reviewed in section 3.10 below.

The water was analyzed by partitioning with dichloromethane and characterizing the activity in the dichloromethane and aqueous phases.

Standard LSC, TLC, LC, HPLC, GLC, GLC-MS and high voltage electrophoresis (HVE) techniques were used.

Results

Distribution of CGA 48 988 and its degradation products in soil incubated under aerobic, aerobic/anaerobic and sterile/aerobic conditions. (Values given in % of the dose applied.)

	Aerobic							Anaerobic		Sterile		
	%							%		%		
days after treatment	0	14	31	66	89	181	360	66	89	31	66	89
Extractable	97.0	97.6	89.4	79.3	67.0	41.4	30.3	91.40	84.90	95.10	94.3	92.2
CGA 48 988	97.9	82.0	59.9	25.7	19.1	4.8	<2.0	49.4	32.5	94.0	90.6	91.7
CGA 42 447	-	-	-	-	-	-	0.5	-	-	-	-	-
CGA 62 826	-	15.6	29.5	53.6	47.9	32.9	23.0	42.0	52.4	0.6	2.7	0.5
Polar	-	-	-	-	-	3.7	4.8	-	-	0.5	1.0	-
Non-extractable	2.1	3.7	6.3	14.1	19.8	37.3	38.3	9.3	8.4	3.2	4.7	4.3
CO_2	-	0.4	0.9	2.9	5.4	15.2	25.3	0.8	0.9	0.1	0.1	0.2
Total	100.0	101.7	96.6	96.3	92.2	93.9	93.9	100.5	94.2	98.4	99.1	96.7

Conclusions

1) The parent CGA-48988 degrades in soil under aerobic conditions with a halflife of about 40 days. The second and third halflives occur at about 80 and 120 days, respectively. CGA-62826 is the only major soil degradation product formed and it represents a maximum of 53.6% of the applied at 66 days of incubation but thereafter also degrades until it is 23% of the applied at 360 days. A polar fraction is found between 6 and 12 months of incubation at levels of 3.7-4.8% of the applied and CGA-42447 is found only after 12 months of incubation at 0.5% of the applied.

   After 66 days incubation, as the degradation product CGA-62826 begins to decline and the parent continues to degrade, the amount of $^{14}CO_2$ and non-extractable activity produced increases. After 6 months of incubation most of the applied activity is divided between $^{14}CO_2$ (15.2%) and non-extractable forms (37.3%) and at 12 months respective levels of 25.3% and 38.3% are reached.

2) Degradation of CGA-48988 is slower under anaerobic conditions than under aerobic conditions with a halflife of about 66 days. CGA-62826 is the only major degradation product representing just over half (52.4%) of the applied activity at 89 days and the amount formed continues to increase between 66 and 89 days. (Note that under aerobic conditions between days 66 and 89, the % CGA-62826 declines). Production of $^{14}CO_2$ is not a major route of anaerobic degradation of the parent and non-extractable residues do not exceed 10% and do not increase with time.

3.6 Leaching Model Study with the Fungicide CGA-48988 in Four Standard Soils, project report 30/76, Basle, Sept. 27, 1976.

An aqueous suspension of CGA-48988 50WP containing 1% radiolabled parent and an aqueous suspension of Telvar 80WP (monuron) were added to the tops of 30 cm. soil columns at 5 kg ai/ha (4.5 lb ai/acre). Then, over 2 days, 200 mm of water was applied to each column via a

pump and, after percolation, the eluate and the soil (in 2 cm. sections) were analyzed for radioactivity via liquid scintillation counting methods and monuron via a published residue method.

The four soils used in the columns are described below.

Origin	pH	Organic Matter %	$CaCO_3$ %	Mechanical Analysis		
				Clay %	Silt %	Sand %
Collombey VS, Switzerland	7.8	2.2	11.5	2.8	10.2	87.0
Lakeland, Florida, U.S.A.	6.6	0.4	0	0.4	0.5	99.1
Les Evouettes VS, Switzerl.	6.1	3.6	0	12.2	49.4	38.4
Vetroz VS, Switzerland	6.7	5.6	15.0	22.6	19.6	57.8

1) Results

Depth of soil layer (cm)	Percentages of CGA-48988 recovered in the various soils and layers			
	Collombey	Evouettes	Vetroz	Lakeland
0 - 2	0.6	1.4	3.2	1.0
2 - 4	0.4	0.8	5.6	0.4
4 - 6	0.4	1.0	8.3	<0.4
6 - 8	0.5	1.9	17.0	0.4
8 - 10	0.5	2.6	44.5	0.4
10 - 12	0.7	2.6	16.5	<0.4
12 - 14	0.7	6.8	1.1	<0.4
14 - 16	1.3	4.7	<0.4	<0.4
16 - 18	1.5	19.0	<0.4	<0.4
18 - 20	2.1	17.7	<0.4	<0.4
20 - 22	2.7	17.6	<0.4	<0.4
22 - 24	4.0	10.9	<0.4	<0.4
24 - 26	5.4	2.7	<0.4	0.5
26 - 28	7.7	<0.4	<0.4	0.5
28 - 30	12.1	<0.4	<0.4	0.8
Leachate	57.7	0.6	<0.4	92.0
Total percentage recovered	98.3	90.3	96.2	96.0

2)

Depth of soil layer (cm)	Percentages of monuron recovered in the various soils and layers			
	Collombey	Evouettes	Vetroz	Lakeland
0 - 2	3.9	6.2	21.1	5.0
2 - 4	0.4	4.3	39.4	2.7
4 - 6	1.6	5.9	30.0	3.5
6 - 8	1.9	10.2	<0.5	3.1
8 - 10	3.5	15.6	<0.5	3.9
10 - 12	3.1	21.8	<0.5	2.7
12 - 14	6.2	24.2	<0.5	3.5
14 - 16	8.2	6.7	<0.5	4.3
16 - 18	11.3	<0.5	<0.5	4.6
18 - 20	13.7	<0.5	<0.5	3.5
20 - 22	17.6	<0.5	<0.5	3.9
22 - 24	15.0	<0.5	<0.5	4.6
24 - 26	5.5	<0.5	<0.5	3.9
26 - 28	<0.5	<0.5	<0.5	4.6
28 - 30	<0.5	<0.5	<0.5	4.6
Leachate	<0.5	<0.5	0.5	33.3
Total percentage recovered	91.9	94.9	90.5	91.7

Conclusions

Ridomil leaches at a very high rate in sandy soils but leaches less in soils of increasing organic matter content.

3.7 Leaching Characteristics of Aged ^{14}C-CGA-48988 (Ridomil) Residues in Two Standard Soils, project report 33/78, Basle, June 10, 1978

Phenyl ^{14}C labeled CGA-48988 was added to Collombey sand and Les Evouettes silty loam soils resulting in concentrations of 5.6 and 8.4 ppm, respectively. The soils were then moistened to 50% capacity and aged in the dark, aerobically, at 25°C for 30 days. Soil aliquots were analyzed at 30 days aging and then aliquots of the aged fortified soils were overlayered on 28cm tall, packed soil columns. One-half inch of water was then added to the columns daily for 45 days.

The soil was analyzed by extracting with methanol: water and measuring for extractable activity by LSC and by combusting the extracted soil.

Eluates were extracted with dichloromethane followed by acidifying the aqueous layer with HCl and again extracting with dichloromethane followed by diethylether. Extracts were analyzed by TLC.

ORIGIN AND PROPERTIES OF SOILS USED FOR "AGED RESIDUE" LEACHING EXPERIMENT

Origin	pH	Organic Matter %	Cation Exchange Capacity meg/10 g soil	$CaCO_3$ %	Mechanical Analysis %Clay	%Silt	%Sand
Collombey, VS, Switzerland	7.8	2.2	14.0	11.5	2.8	10.2	87.0
Les Evouettes, VS, Switzerland	6.1	3.6	9.0	0	12.2	49.4	38.4

Conclusions

1) After 30 days of aerobic aging 97.4% and 99.2% of the activity was extractable from the sandy and silt loam soils, respectively.

2) Results after leaching in % applied ^{14}C

soil	remaining in soil	eluate
sandy	16.1	79.2
silty loam	34.9	48.7

3) About 70% of the activity remaining in the soil was extracted with methanol: water.

4) Of the activity found in the eluate of the sandy soil, 56% was parent, 31% was CGA-62826, 1% was an unknown polar metabolite and 12% was unaccounted. In the eluate of the silty loam soil 70% was parent, 18% was CGA-62826, 1% was the unknown polar metabolite and 11% was unaccounted.

3.8 Volatilization of CGA-48 988 from Soil Under Laboratory Conditions, project report 29/77, May 27, 1977, pages 57-76.

Samples of oven dry soil were fortified at levels between 45 and 182 ppm, moistened to 12%, placed in flasks maintained at various temperatures over which water saturated air was drawn at different rates.

After passing over the soil, the air was bubbled through ethylene glycol to trap the pesticide which was then extracted with methylene chloride. The methylene chloride was evaporated, the residue redissolved in acetone and then analyzed for parent by GC with a PN detector.

A parallel test was run using ^{14}C labeled material for recovery and material balance data.

TABLE III CHANGES OF SOIL MOISTURE AND VOLATILIZATION RATE UNDER VARIOUS EXPERIMENTAL CONDITIONS

Soil type	temperature	initial soil concentration	air flow rate	soil-moisture %		volatilization rate
	^{o}C	ug x g^{-1}	l x h^{-1}	start	end	kg x ha^{-1} x day^{-1}
Collombey	35	120	30	12	11.0	0.010
	35	120	60	12	9.7	0.019
	45	120	30	12	9.1	0.043
	35	160	30	12	11.6	0.015
Evouettes	35	120	30	12	-	0.006

)PERTIES OF SOILS FOR VOLATILIZATION EXPERIMENTS

organic matter	water capacity	mechanical analysis clay	silt	sand
%	%	%	%	%
2.2	22	2.8	10.2	87.0
3.6	38	12.2	49.4	38.4

N OF CGA-48988 FROM SOIL AT DIFFERENT EXPERIMENTAL CONDITIONS

air flow rate	initial soil* concentration	amount volatilized after 48 hours		volatilization rate	
$l \times h^{-1}$	$ug \times g^{-1}$	^{14}C $[ug \times cm^{-2}]$	GLC	$ng \times ^{14}C \times cm^{-2} \times h^{-1}$	GLC
30	40	0.16	0.06	3.3	1.3
30	80	0.29	0.15	5.9	3.0
30	120	0.38	0.20	8.0	4.1
30	160	0.52	0.29	10.8	6.0
30	120	-	0.86	-	18.0
30	120	-	3.73	-	76.0
15	120	-	0.12	-	2.6
60	120	-	0.37	-	7.8
30	120	0.24	0.12	5.1	2.4

Conclusions

1) The volatilization rate is directly proportional to the initial soil concentration of CGA-48988, the soil temperature, the air flow rate across the soil surface and is inversely proportional to greater soil adsorption capacities.

2) Under typical use conditions, less than 0.5% of the applied would be lost due to volatilization.

3.9 Adsorption and Desorption of CGA-48988, (Ridomil) in Various Soil Types, proj. report 35/78, Basle, June 15, 1978

Dried samples of 4 soils were shaken with aqueous solutions of ^{14}C - labeled CGA-48988 at 1-10 ppm concentrations for 24 hours at 20°C and then centrifuged. The supernatant was analyzed for activity and the amount of CGA-48988 adsorbed was calculated by difference.

Desorption was determined by shaking the decanted soil with distilled water for 24 hours at 20°C, centrifuging and analyzing the supernatant and then repeated the procedure.

The Freundlich adsorption isotherm was used in the adsorption/desorption calculations.

Origin and properties of soils used for adsorption/description measurements

Origin	pH	$CaCo_3$ %	Organic Matter %	Cation exchange capacity (meg/100 g soil)	Mechanical Analysis		
					Clay %	Silt %	Sand %
Collombey VS, Switzerland	7.8	11.5	2.2	14.0	2.8	10.2	87.0
Lakeland, Florida, U.S.A.	6.3	0.1	1.2	3.7	1.5	2.1	96.4
Les Evouettes VS, Switzerland	6.1	0	3.6	9.0	12.2	49.4	38.4
Vetroz VS, Switzerland	6.7	15.0	5.6	29.4	22.6	19.6	57.8

Results

1) FREUNDLICH ADSORPTION CONSTANTS OF CGA 48988 IN COMPARISON TO THOSE OF SOME OTHER PESTICIDES.

Soil Type / Compound	Collombey		Lakeland		Evouettes		Vetroz	
	k*	$\frac{1}{n}$	k*	$\frac{1}{n}$	k*	$\frac{1}{n}$	k*	$\frac{1}{n}$
CGA 48988	0.43	0.83	0.48	0.79	0.87	0.77	1.40	0.83
Atrazine	0.86	0.88	-	-	1.98	0.93	2.88	0.92
Ametryn	1.52	0.85	-	-	4.55	0.83	7.68	0.86
Methidathion	2.35	0.80	-	-	3.89	0.79	10.8	0.82
Diazinon	5.60	0.63	-	-	11.7	0.77	23.4	0.93

*ug adsorbed per g of soil

2) DESORPTION OF CGA 48988 FROM VARIOUS SOIL TYPES

Soil Type	Initial Concentration ug/ml	Amount adsorbed ug/g	Desorption with Water (ug/g) 1st	2nd	Total	%	Amount adsorbed after 2nd Desorption ug/g	%
Evouettes Silty	1.0	0.66	0.29	0.13	0.42	63.6	0.15	22.4
Loam	2.5	1.30	0.76	0.27	1.03	79.2	0.22	16.9
	5.0	2.46	1.56	0.43	1.99	80.9	0.42	17.2
	10.0	4.32	2.82	1.12	3.94	91.2	0.85	19.8
Lakeland Sand	1.0	0.41	0.18	0.04	0.22	53.7	0.15	35.7
	2.5	0.83	0.46	0.13	0.59	71.1	0.24	29.5
	5.0	1.46	0.75	0.31	1.06	72.6	0.40	27.5
	10.0	2.78	1.33	0.44	1.77	63.7	0.92	33.1
Collembey Sand	1.0	0.36	0.22	0.04	0.26	72.2	0.09	23.8
	2.5	0.75	0.47	0.08	0.55	73.3	0.17	22.9
	5.0	1.35	0.95	0.22	1.17	86.7	0.15	11.5
	10.0	2.61	1.88	0.46	2.34	89.6	0.37	14.0
Vetroz Sandy Loam	1.0	1.07	0.47	0.06	0.53	49.5	0.45	42.2
	2.5	2.43	1.12	0.21	1.33	54.7	0.96	39.5
	5.0	4.40	2.19	0.51	2.70	61.4	1.86	42.4
	10.0	7.78	4.19	0.97	5.16	66.3	3.55	45.7

Conclusions

Soil adsorption of Ridomil is minor. This is supported by the leaching results which show Ridomil to be a strong leacher.

3.10 Distribution and Degradation of CGA-48988 (Ridomil) in a Field Soil, project report 55/77, Basle, October 13, 1977

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After planting a 1.38 m^2 plot in Switzerland with three rows of potatoes, the plot (65.8% sand, 17.3% silt, 16.9% clay, 2.5% OM and pH = 6.9) was treated with ^{14}C ring labeled CGA-48988 at an equivalent rate of 3.65 lb ai/A using the 50WP formulation.

Soil cores of 30 cm. depth were taken just after treatment and at 25%, 50%, 75% and 100% of crop maturity and at one year after treatment. These sampling times correspond to 0, 33, 54, 81, 103 and 355 days post-application.

The soil was extracted separately with methylene chloride followed by methanol/water (8:2). The methanol was evaporated from the methanol/water extract and the remaining aqueous solution was partitioned into methylene chloride and aqueous phases. The resulting aqueous phase, after acidification to pH 2, was again partitioned into methylene chloride and aqueous phases. This final methylene chloride phase was subjected to methylation to identify CGA-62826. Previous methylene chloride phases were analyzed for parent compound and other degradation products.

Standard combustion and liquid scintillation counting procedures were used in addition to TLC, LC, HPLC, GLC, GLC/MS and high voltage electrophoresis (HVE).

Results

Distribution of CGA 48 988 and of its degradation products in a field soil (in % of the dose applied)

Days after application	Radioactive fraction	Soil layers (cm) 0 - 7.5	7.5 - 15	15 - 30	Recovery
0	CGA 48 988	98.6	6.0	8.2	112.8
	Non-extractables	-	-	-	-
	Total	98.6 (5.6)	6.0 (0.4)	8.2 (0.3)	112.8
33	CGA 48 988	16.0	7.0	5.1	28.1
	CGA 62 826	6.3	3.9	3.8	14.0
	Unpolar X_1			0.9	0.9
	Non-extractables	5.7	3.2	5.3	14.2
	Total	28.0 (1.75)	14.1 (0.88)	15.1 (0.42)	57.2
54	CGA 48 988	7.3	4.4	1.7	13.4
	CGA 62 826	2.4	2.6	1.4	6.4
	Non-extractables	9.8	5.3	3.1	18.2
	Total	19.5 (0.93)	12.3 (0.72)	6.2 (0.27)	38.0
81	CGA 48 988	4.8	4.1	2.7	11.6
	CGA 62 826	0.2	1.1	1.0	2.3
	Non-extractables	8.3	7.0	5.3	20.6
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Conclusions

1) The halflife of the parent in soil under field conditions is about 2 weeks. CGA-62826 is the major soil degradation product formed, peaking during the first month at possibly 20% of the initial activity and then declining to 0.5% of the applied at 1 year.

2) Non-extractable activity is expected to increase steadily for the first 3-4 months to 20-25% of the initial dose, but will then decline to half of that level at one year.

3) Two minor products, one polar and one non-polar form in soil but are always less than 1% of the applied.

4) In this study, the recovered activity dropped from 38% to 13% of the applied at 54 and 355 days, respectively. The activity not accounted for is presumably lost due to $^{14}CO_2$ production and/or leaching beyond the sampling depth.

3.11 Distribution of the Non-Extractable Radioactivity between Different Soil Organic Matter Fractions of a Field Soil Treated with ^{14}C - Labeled CGA-48988 (Addendum to Project Report 55/77), project report 56/77, Basle, October 13, 1977.

The non-extractable soil residue from the study titled "Distribution and Degradation of CGA-48988 (Ridomil) in a Field Soil" after 355 days of incubation and reviewed above, 3.10, was fractionated.

Results

1) Fractionation of the non-extractable residues in various layers of ^{14}C-CGA 48988 treated soil.

	Soil Layer (cm)		
	0 - 7.5	7.5 - 15	15 - 30
Acid washing	3.7	2.9	3.9
Humin	34.0	40.4	50.8
Humic acid — soluble in alcohol *	1.1	0.4	0.3
Humic acid — insoluble in alcohol	23.8	27.2	14.8
Fulvic acid — soluble at pH 4.8	31.6	27.1	16.3
Fulvic acid — insoluble at pH 4.8**	5.8	2.0	13.9
Total = Non-extractable	100.0	100.0	100.0
Total in % applied	3.7	4.0	3.0

* Hymatomelanic acid
** β - Humus

Conclusions

1) 97.5% of the non-extractable soil residue at 355 days (10.7% of the applied) is not soluble in 0.1 N HCl but only 1/2 is soluble in 0.5 N NaOH. This base soluble activity is distributed between the humic and fulvic acids in the ratio 2:3.

   (See the study titled "Distribution and Degradation of CGA-48988 (Ridomil) in a Field Soil" reviewed in section 3.10 above, to which this study is an addendum.)

3.12 Uptake and Balance of Ø-^{14}C-CGA-48988 and its Metabolites in Greenhouse Grown Bright and Burley Tobacco, report #ABR-78036, pg. 211, acc.# 234438.

A Georgia sandy loam soil (87.2% sand, 9.6% silt, 3.2% clay, 2.3% OM, pH = 5.0) was placed in 5-gallon buckets. Twenty of the buckets were planted with one tobacco seedling each and the soil around five of the seedlings was treated with 19 mg. Ø-^{14}C-CGA-48988 (equivalent to 0.25 lb ai/A based on 6000 plants/acre) while the soil around the other 15 seedlings was treatedwith 38 mg. Ø-^{14}C-CGA-48988 (equivalent to 0.50 lb ai/A). Plants were watered daily and fertilized every six days.

In a parallel study, Ø-^{14}C-CGA-48988 was pre-plant incorporated by overlayering on untreated soil in a bucket, 3" of fortified soil, resulting in each bucket receiving 44.8 mg of ^{14}C-ai. (Each bucket had 0.63 feet^2 surface area). This rate corresponds to 6.8 lb ai/A broadcast (which is in disagreement with the figure of 3.15 lb ai/A broadcast calculated by the registrant. See "Report of Telephone Call or Visitor" to PM 21 dated November 29, 1978 in which the registrant concurs with the figure of 6.8 lb ai/A. Tobacco seedlings were than planted in the soil).

Tobacco leaves and soil cores (0-3", 3-6", 6-11") were sampled at 3, 6 and 12 weeks after transplanting.

Details of the soil extraction and combustion methods were referenced but not submitted. See section 3.2 above, for validation of the results.

BALANCE AND CHARACTERIZATION OF ϕ-^{14}C-CGA-48988 IN TREATED GREENHOUSE SOIL - BURLEY TOBACCO (6.8 lb. a.i./a pre-plant incorporated).

THI* (weeks)	0			3			12		
Depth (inches)	0-3	3-6	6-11	0-3	3-6	6-11	0-3	3-6	6-11
PPM	6.53	1.57	--	4.94	1.65	0.20	2.88	2.70	0.41
Balance	Percent of Total ^{14}C in Soil Sample								
Organic	84.4			77.6			31.8	31.4	
Aqueous	1.5			2.3			3.9	4.6	
Nonextractable	15.4			28.6			42.5	46.7	
TLC Characterization									
CGA-48988	80.1			65.4			28.8	31.7	
CGA-62826	<0.3			1.1			2.8	6.0	
Unknowns 1	--			--			0.5	0.5	
2	--			--			1.3	1.7	

*THI = Treatment to harvest interval.

^{14}C-EQUIVALENT TO CGA-48988 IN GREENHOUSE SOIL - BRIGHT TOBACCO - (transplant water treatment)

Rate (lb. ai/a)	0.25									0.5								
THI* (weeks)	0			6			12			0			6			12		
Depth (inches)	0-3	3-6	6-11	0-3	3-6	6-11	0-3	3-6	6-11	0-3	3-6	6-11	0-3	3-6	6-11	0-3	3-6	6-11
PPM	13.7	0.7	0.3	2.2	0.7	0.2	1.1	0.6	0.2	17.4	3.6	0.8	3.8	2.2	0.6	2.3	1.3	0.4

*THI = Treatment to harvest interval.

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Conclusions

1) According to the registrant CGA-48988 is metabolized in the treated tobacco plant to approximately 25 different metabolites with CGA-62826 being the only one identified. It is never more than 1.5% of the activity in the plant.

2) CGA-48988 and its soil residues show some leaching.

3) Between 3 and 12 weeks in the soil, the parent degrades to primarily non-extractable material.

4) At 12 weeks, 20% of the applied is not found. Loss may be attributed to formation of volatile ^{14}C degradation products via ring cleavage or leaching beyond the 11" sampling depth (the depth of the buckets was not given).

5) One soil degradation product, CGA-62826, was identified. It represents 1% of the applied at 3 weeks and 8.8% at 12 weeks. There is also some unidentified extractable activity, representing 3% of the applied, at 12 weeks.

3.13 Balance and Metabolism of Ø-^{14}C-CGA-48988 in Potatoes, report no. ABR-78001, January 5, 1978.

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Two 7 foot rows of white potatoes in a 3' x 10' field plot were sprayed over the top with ^{14}C-ai three times beginning six weeks after emergence and followed at 28 day intervals at a rate of 1.1 lb ai/A/treatment. Tubers, stalks and soil samples were taken immediately before and after each treatment and at maturity (18 weeks after planting).

Soil aliquots of 1 gram were combusted and aliquots were extracted according to AG-254 (not submitted). Metabolites were characterized by standard radio TLC techniques.

The soil was a silt loam of 44.4% sand, 44.0% silt, 11.6% clay, 1.8% OM and pH = 5.5. The test was run in Red Hook, New York.

Results

BALANCE OF RADIOACTIVITY IN SOIL FROM A FIELD PLOT SPRAYED WITH ϕ-^{14}C-CGA-48988

Interval (weeks)*	6 (0)	10 (4)						14 (8)						18 (12)		
		pre			post			pre			post					
Depth (inches)	0-3	0-3	3-6	6-9	0-3	3-6	6-9	0-3	3-6	6-9	0-3	3-6	6-9	0-3	3-6	6-9
Total ppm	1.36	0.48	0.42	<0.01	3.49	0.02	<0.01	2.00	0.06	0.01	2.72	0.11	0.02	2.62	0.08	0.23
Balance in 0-3" Layer (%)																
Organic	100.0	86.9			90.7			57.1			75.1			82.7		
Aqueous	0.0	0.0			1.8			15.2			5.7			3.3		
Nonextractable	4.0	19.0			7.5			21.7			13.4			24.1		
Total	104.0	105.9			100.0			94.0			94.2			110.1		
Characterization of Radioactivity in the Organic Fraction (%)																
CGA-48988	99	74.3			87.9			52.7			70.7			70.9		
CGA-62826	0	12.6			2.8			4.4			4.4			11.8		
Total	99.0	86.9			90.7			57.1			75.1			82.7		

*Numbers in parentheses indicate weeks after the first application of ϕ-^{14}C-CGA-48988 (May 17, 1977).

Conclusions

1) The parent compound degrades in soil with a halflife of about 6-8 weeks. However, repeated applications and lack of rainfall will extend the halflife. The only degradation product identified is CGA-62826 and non-extractable activity is seen to increase with time.

2) Since this study involved repeated applications the fate of the parent and formation of degradation products could not be monitored as after a single application.

3) Leaching, as a route of dissipation of CGA-48988 residues, cannot be determined since rainfall data was not reported.

4) The registrant reports that CGA-48988 metabolizes in the potato plant.

3.14 Uptake of Ø-^{14}C-CGA-48988 in Potatoes Grown Grown in a Field Plot -Preparation of Rotational Plots, report no. ABR-78013, Jan. 24, 1978.

Two 19 foot rows of white potatoes were treated 6 weeks post-emergence with an EtOH:H_2O (1:1) solution of Ø-^{14}C-CGA-48988 at 0.4 lb ai/A and then five more times at 14 day intervals. Mature tubers were sampled at 1 day after the last treatment and 14 days thereafter, washed, homogenized and combusted.

Soil cores were taken before and after each treatment and at each potato harvest and analyzed according to AG-233 and AG-254 (with extractable soil activity analyzed by radio TLC). Also, soil aliquots were combusted.

The soil was a silt loam of 44.4% sand, 44.0% silt, 11.6% clay, 1.8% OM and a pH = 5.5. The study took place in Red Hook, New York.

Results

1) BALANCE OF RADIOACTIVITY IN 0-3" SOIL FROM FIELD PLOT SPRAYED WITH ϕ-^{14}C-CGA-48988

Interval (Weeks)	6	8		10		12	
		Pre	Post	Pre	Post	Pre	Post
Total ppm	0.59	0.51	1.12	0.78	1.10	1.12	1.49
Balance (%)							
Organic	93.4	75.3	90.8	71.0	89.0	64.1	74.8
Aqueous	7.7*	9.0*	7.6	9.5	7.4	12.0	8.5
Non-Ext.	3.4	14.2	9.2	16.9	11.7	16.5	15.2
	96.8	89.5	107.6	97.4	108.1	92.6	98.5

Interval (Weeks)	14		16			18
	Pre	Post	Pre	Post	PHI-1	PHI-14
Total ppm	2.01	1.86	0.30	1.13	1.66	1.82
Balance (%)						
Organic	76.6	71.7	79.8	94.5	69.7	82.3
Aqueous	10.5	10.5	15.1*	4.7	12.8	7.0
Non-Ext.	20.1	19.6	11.2	6.7	20.3	4.1
	107.2	101.8	91.0	105.9	102.8	93.4

Characterization of PHI-14 soil extractable ^{14}C	% of Total ^{14}C
CGA-48988	68.7
CGA-62826	19.8

* Numbers too low for reliable quantitation.

2) Formation and identification of metabolites in the potato plant were not addressed in this study.

Conclusions

1) Degradation of the parent is occurring in the soil as made evident by the increase in non-extractable and aqueous soluble activity. Because of the repeated applications, the halflife and rate of degradation cannot be derived.

2) Repeat applications will result in residues of the parent being present in the soil at higher levels and longer into and perhaps beyond the growing season.

3.15 Distribution, Degradation and Excretion of CGA-48988 in the Rat, acc.# 234431, pg. 72-90.

Rats were given ^{14}C-ring labelled Ridomil at 0.5 mg/kg and 25 mg/kg via stomach intubation.

Urine, feces and expired CO_2 were collected during 144 hours post-treatment and then the rats were sacrificed for organ and tissue analysis.

Results

1) Fate of ^{14}C-activity in Rats - %

	Male	Female
Urine	37	55-63
Feces	63-66	35-45
Expired Air	0.5	0.01
Tissue Residues	0.1	0.1-0.2
Cage Wash	0.3-0.7	0.4-1.7

2) There were 4-6 major metabolites in the urine plus 10 minor ones. The metabolites were polar. No parent compound was found in the urine.

3.16 Metabolism of CGA-48988 in the Rat, proj. report 26/78, Basle, May 12, 1978.

Female rats were given 27.9 mg/kg of ^{14}C ring labeled CGA-48988 and the urine and feces were collected for 48 hours post-treatment for metabolite identification.

Results

1) Hours after treatment

Hours after treatment	% dose excreted		
	Urine	Feces	Total
0-24	54.0	21.1	75.1
24-48	9.5	11.7	21.2
total	63.5	32.8	96.3

2) The urinary metabolite is similar to that found in the rat metabolism study in 3.15 above.

3) The following urinary metabolites were identified:

a) CGA-62826 and its glucuronic acid conjugate
b) CGA-67868
c) CGA-37734 and its glucuronic acid conjugate
d) N-(2-methyl-6-hydroxymethyl-phenyl)-N-(methoxyacetyl) - alanine methyl ester and its glucuronic acid conjugate

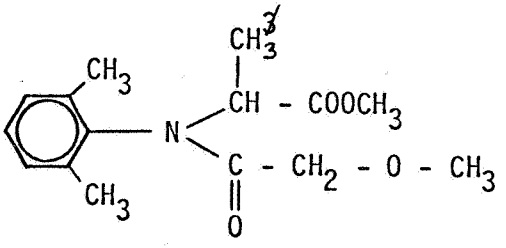
The only fecal metabolite identified was CGA-62826 and its glucuronic acid conjugate.

4) Structures are given below in section 3.17.

5) Metabolism of the parent proceeds through

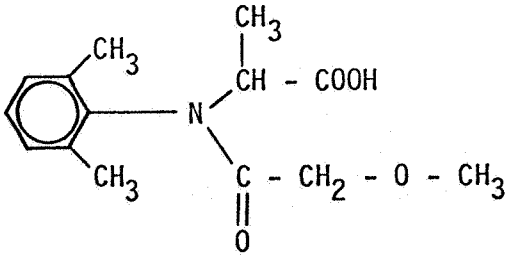
a) methyl ester hydrolysis
b) N-dealkylation
c) methyl ether cleavage
d) benzylic methyl oxidation

3.17 Parent, degradation products and where they occur

Structure	where occurs
	

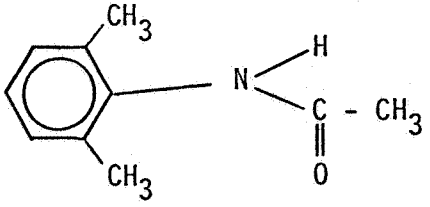
parent

N-(2,6-dimethylphenyl)-N-(methoxyacetyl)-alanine methyl ester



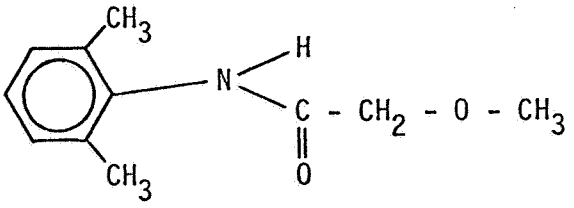
soil (aer. & anaer.)
rats (urine and feces)
hydrolysis at pH 1, 9, 10 at > 50°C
potato stalks
tobacco

CGA-62826
N-(2,6-dimethylphenyl)-N-methoxyacetyl)-alanine



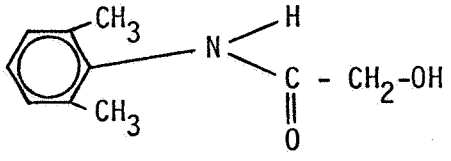
soil (aer) - minor

CGA-42447 2,6-dimethylacetanilide



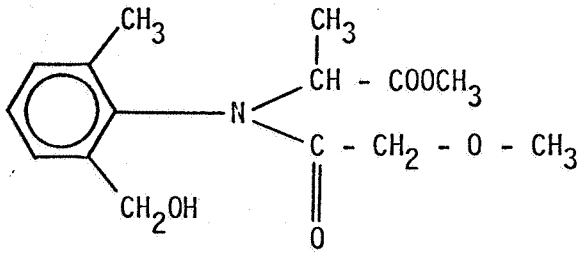
rats (urine)

CGA-67868
N-(2,6-dimethylphenyl)-N-(methoxyacetyl)-alanine



rats (urine)

CGA-37734
N-(2,6-dimethylphenyl)- N-
(hydroxyacetyl) alanine



rats (urine)

N-(2-methly-6-hydroxymethylphenyl)-
N-(methoxyacetyl)-alanine

4. CONCLUSIONS

4.1 Environmental Profile

Under conditions likely to be found in the environment, Ridomil will be stable to hydrolysis and soil surface photolysis. In soil, under aerobic conditions, Ridomil can be expected to degrade with a halflife of about 7 weeks with the acid product, CGA-62826, being the principle product, which in turn will break down to non-extractable material and CO_2. Under anaerobic soil conditions Ridomil also will break down, but with a halflife of about 9 weeks with CGA-62826 again being the major product but persisting longer than under aerobic conditions. Ridomil is stable in sterile soil, indicating soil microbes contribute to its breakdown under non-sterile conditions.

Ridomil and its aged soil residues are highly mobile via leaching in sandy soils low in organic matter but loss of Ridomil due to volatilization is not expected. Also, soil adsorption of Ridomil is minor, as supported by its high leachability.

Under field conditions, the fate of Ridomil in soil is similar to that under lab conditions as described above except for the shorter halflife of two weeks under field conditions.

One of Ridomil's proposed uses is in Florida citrus nurseries where the soils are presumably sandy. Ridomil is expected to leach in such sandy soils and possibly contact fish. Without a fish accumulation study, hazards to fish cannot be assessed.

4.2 The following data requirements have been met and will support additional uses of Ridomil:

- hydrolysis
- photolysis (soil surface)
- aerobic soil metabolism
- anaerobic soil metabolism
- effects by microbes
- leaching and aged leaching
- adsorption/desorption
- field dissipation

5. RECOMMENDATIONS

5.1 The fate of Ridomil in the environment is not fully understood, therefore we do not concur with the proposed uses. AMC Apr 3, 1979

The following Environmental Fate studies are needed:

5.1.1. Effects of Ridomil on soil microbes

5.1.2 Fish accumulation

Refer to the July 10, 1978 proposed guidelines for test protocol (FR 43, no. 132)

5.2 To EEB -

Attention is drawn to the high leachability of Ridomil and its aged soil residues in sandy soils low in organic matter and the proposed Florida citrus nursery use. The proposed use may result in residues reaching and accumulating in fish. We defer to EEB for the need of additional EC data to aid in their hazard assessment.

Samuel M. Creeger March 8, 1979

February 26, 1979 Review Section 1
Environmental Fate Branch

HED:RNEY:jem96/smw:RAVEN:x479-2000:3/2/79:01806