

Date Out EFB: JUN 17 1981

*Caswell #1
323EE*

To: Product Manager
TS-767

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

Attached please find the environmental fate review of:

Reg./File No.: 100-ARI, ART

Chemical: CGA-64250

Type Product: Fungicide

Product Name: TILT 3.6E and TILT Technical

Company Name: CIBA-GEIGY

Submission Purpose: registration of technical and on grasses grown for seed

ZBB Code: 3(c)(5)

ACTION CODE: 115

Date in: 2/17/81

EFB # 763, 764

Date Completed: JUN 17 1981

TAIS (level II)

Days

Deferrals To:

61

12

Ecological Effects Branch

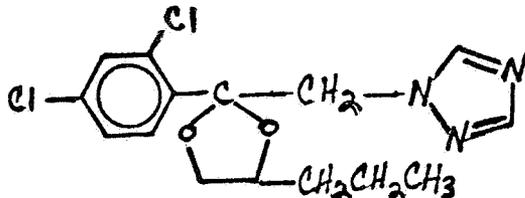
Residue Chemistry Branch

Toxicology Branch

1.0 INTRODUCTION

CIBA-GEIGY has submitted environmental chemistry data in support of the registration of technical CGA-64250 fungicide and the formulation TILT 3.6E use on grasses.

CGA-64250 = TILT, 1-[2-(2',4'-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole



See attached proposed label for directions for use on grasses and for product composition.

2.0 Discussion of Data

- 2.1 "Rate of Hydrolysis of CGA-64250 Under Laboratory Conditions," N. Burkhard, CIBA-GEIGY LTD, Basle, Switzerland, January 30, 1980, Accession No. 244269.

Experimental Procedures

Solutions of 10 ppm ¹⁴C-triazolring-labelled CGA-64250 were prepared in 0.1M HCl, 0.1N NaOH and pH 5 (phthalate), pH 7 (phosphate), and pH 9 (borate) buffers which were sealed in flasks and shaken in the darkness at 70 °C for up to 672 hours. Sampled aliquots were shaken with isopropyl ether and the extracts were analyzed by GLC-PN. Recoveries were 100 ± 3% into the ether.

Results

No hydrolysis was observed under any conditions.

Conclusions

This is an acceptable study that shows that CGA-64250 is very resistant to hydrolysis.

- 2.2 "Photolysis of CGA-64250 on Soil Surface Under Artificial Sunlight Conditions," N. Burkhard, CIBA-GEIGY LTD, Basle, Switzerland, March 24, 1980, Accession No. 244269.

¹⁴C-triazolring-labelled CGA-64250 was applied to dry or moist (12% water) soil (silty loam, pH 6.1, 3.6% OM, 12.2% clay, 49.4% silt, 38% sand), which was placed in metal boxes layered 0.6 cm deep exposed to artificial sunlight in a Hanau Suntest apparatus (>290 nm light at 940±50 J.M⁻².S⁻¹). Soil samples were exhaustively extracted with methanol and with acetone, and the extracts analyzed by GLC-PN and by TLC/liquid scintillation.

1.2 Results

After an exposure interval of 24 hours, 96.5% of the CGA-64250 was recovered from the dark controls and 97.5% from the exposed dry soil. In the moist samples, 92% was found in the dark samples and 91.5% in the exposed soil.

Conclusions

The study demonstrates that CGA-64250 does not photodegrade on soil surfaces to any appreciable extent over a 24 hour exposure. The exposure interval is rather short to discern the long-term degradation on soil, but the 1978 guidelines do not give guidance in this regard. The study therefore satisfies EFB data requirements.

- 2.3 "Adsorption and Desorption of CGA-64250 in Various Soil Types", N. Burkhard, CIBA-GEIGY LTD, Basle, Switzerland, August 14, 1980, Accession No. 244269

Experimental Procedures

Ten to 50g oven dry soil (see Table for characteristics) were mixed in centrifuge tubes with 100 ml of 1.0 to 10.0 ppm ^{14}C -CGA-64250, and shaken over night at 20°C. The mixtures were filtered through paper and the amount of ^{14}C remaining in the water was measured by scintillation counting. The soil was resuspended in distilled water and shaken for 3 days at 20°C and assayed as above.

Results

The data were described as linear Freundlich isotherms. The adsorption constants ranged from 8.48 to 59.0 (see accompanying Table). The results also show the desorption is not completely reversible.

Conclusions

This is a valid study which satisfies environmental chemistry data requirements and indicates that CGA-64250 is fairly tightly bound to soil.

- 2.4 "Effects of Soil Application of CGA-64250 on Nitrification, Soil Respiration, and Nitrogen, Fixation, E.J. Butterfield, G.P. Karcich and S. Fox Boyce Thompson Institute, Ithaca, N.Y. November 114, 1979. Accession No. 244269.

Experimental Procedures

Two soils were used, both were clay loam with organic matter of less than 1%. One was from the CIBA-GEIGY research farm in Mississippi and the other from a C-G farm in Nebraska. A mechanical analysis will be provided in the future. The microbial populations of the soil were measured before starting the studies and found to be in the normal range; bacteria were 4.45×10^7 CFU/g (Mississippi) and 7.64×10^7 CFU/g (Nebraska), actinomycetes were 7.18×10^4 CFU/g (Miss.) and 9.8×10^4 CFU (Neb), fungi were 6.01×10^4 CFU/g (Miss.) and 7.35×10^4 CFU (Neb.).

Nitrification (conversion of NH_4^+ to NO_3^-)

The soils were mixed with an equal weight of sand. The treatments of soil (weight CGA-64250 to weight soil) included the addition of 1.4 g ammonium sulfate and 0.47 calcium carbonate to the 2.7 kg soil. A treated control using 100 ppm sodium azide was used although the untreated control samples were lost. The soils were brought to a water content of 18% and were incubated at $23 \pm 2^\circ\text{C}$ under ambient lab conditions. Samples were taken at 0 - 28 days; aqueous extracts of soil samples were taken and the concentration of nitrate ion was measured with a specific electrode.

Respiration

The soils described above were amended by the addition of 1% dry alfalfa.

In addition to the treated samples, treated (azide) and untreated controls were prepared. Soils were brought to 18% water content. Until the sampling time, the samples were incubated in the open air. At sampling, flasks were purged with air, and then sealed for up to one hour, during which time, air samples were withdrawn and CO_2 measured in an infrared gas analyzer.

Nitrogen Fixation

The above soils were amended with up to 100 ppm CGA-64250 or left as untreated controls and placed in pots which were planted with 3 soybean seeds and maintained at 22°C (day) and 18°C (night) with a 14 hour photo period. The effect of nitrogen fixation was measured using the standard assay of the conversion of acetylene to ethylene. Growth effects were measured by quantifying plant dry weights.

Results

Nitrification

Table 1 shows that effects of CGA-64250 were minimal, with the only statistically significant reduction occurring at the 100 ppm level. This effect was discernible even the loss of the untreated control group.

Respiration

As is evident in Table 2, soil respiration was inhibited only at the 100 ppm treatment rate on day 1 after treatment but returned to control levels by day 3.

Nitrogen fixation

Table 3 data shows that CGA-64250 is a strong growth retardant and also inhibited acetylene reduction. These effects were noted even at 1 ppm (in Nebraska soil). This latter effect was attributed to phytotoxicity rather than inhibition of nitrogenase.

TILT CGA-64250 Reviews

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Conclusions

Soil respiration and nitrification were not significantly reduced by treatment with up to 100 ppm CGA-64250. However, growth and nitrogen fixation were markedly reduced by as little as 1 ppm CGA-64250.

- 2.5 "Leaching Model Study with the Fungicide CGA-64250 in Farm Standard Soils, J.A. Gouth, 8/27/78, CIBA-GEIGY LTD, Basle, Switzerland, Accession No. 244269.

Experimental Procedures

¹⁴C-CGA64250 was applied to the top of a 30 cm soil column (see Table 4 for soil characteristics) at a rate of 5kg/ha. Two hundred mm of water were applied over a 2 day period.

Both the eluted water and extracts of column segments were measured for ¹⁴C content by liquid scintillation counting.

Results

As summarized in Table 5, CGA 64250 migrated to a measurable degree in the lakeland (low organic matter) soil with 9.2% appearing in the leachate, and to a lesser extent in the Collombay, Evouettes, and Vetroz soils.

Conclusions

This is a valid study which satisfies environmental chemistry requirement, although a less than optimum amount of eluting water was used. The study demonstrates that CGA-64250 is capable of leaching through sandy soils which are low in organic matter.

- 2.6 "Leaching Characteristics of Aged ¹⁴c-CGA-64250 Residues in Two Standard Soils," A. Keller, CIBA-GEIGY LTD, Basle, Switzerland, November 14, 1979 Accession No. 244269.

Experimental Procedures

Triazole-labelled ¹⁴C-CGA-64250 was applied to the Collombey sand and Les Evouettes silty loam soils (see preceding study for soil characteristics) and the mixture was aged aerobically for 30 days at 25°C. Two cm layer of the treated soils were placed on top of 28 cm columns of untreated soils, which were eluted daily with 16 ml of water for 45 days. Both leachate and extracts of segments of the columns were analyzed by scintillation counting and TLC.

Results

The results are listed in Table 6-11. They demonstrate that leaching of aged residues of CGA-64250 was minimal. Most of the ¹⁴C in the eluates was tentatively characterized by GLC-MS as 1-[2-(2',4'-dichlorophenyl)-4-propanolyl-1,3-dioxolan-2-yl-methyl]-1H-1,2,4-triazole (Metabolite Uz). Given the large volume of eluting water used (240 ml), the amount of leaching is considered low.

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Conclusions

The study satisfies environmental chemistry data requirements for mobility of aged pesticide residues, and demonstrates that only minor amounts of aged CGA-64250 will leach.

- 2.7 "Degradation of CGA-64250 (TILT) in Soil Under Aerobic, Aerobic/Anaerobic and Sterile/Aerobic Conditions", A. Keller, CIBA. GEIGY LTD, Basle, Switzerland, June 24, 1980, Accession No. 244269.

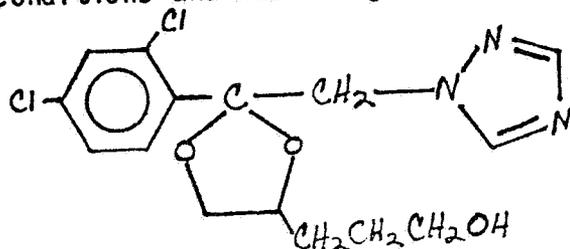
Experimental Procedures

A silty loam soil was collected at Les Barges Switzerland with the following properties; sand 33.5%, silt 61.7% clay 4.8%, organic carbon 2.7%, pH 7.6.

Triazole - ¹⁴C-labelled CGA-64250 was mixed with soil at a rate of 1 ppm based on dry soil weight soil moisture was adjusted to 70% of field capacity and sample flasks were connected to an air flow apparatus (60 ml/min) which terminated with gas absorption bottles (ethylene glycol, sulphuric acid, sodium hydroxide). Incubation was at 25C in darkness. After 30 days of aerobic incubation, anaerobic conditions were established in some of the remaining samples by flooding with water and replacing air with nitrogen. A comparable sterile aerobic control was also run. Samples were extracted, fractionated, and analyzed according to the accompanying figure.

Results

The results listed in Table 12, 13, show that CGA-64250 degrades slowly under aerobic conditions in soil (half-life about 10 weeks) but not under anaerobic or sterile conditions. Most of the material becomes bound to soil. Metabolite U₃ accounted for 23.6% of the ¹⁴C after 52 weeks of aerobic conditions and was assigned the following structure based on GLC-MS analysis:



Conclusions

This study satisfies environmental chemistry data requirements for an aerobic soil metabolism study, and demonstrates that CGA-64250 degrades slowly in aerobic soil.

- 2.8 "Effects of CGA-64250 on the degradation of ¹⁴C-Cellulose, ¹⁴C-protein/and ¹⁴C-starch in soil," R. Mumma and E. Bogus, Pennsylvania State University, University Park, PA, Accession No. 244269.

TILT CGA-64250 Reviews

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Experimental Procedure

Loam and a silt loam soils were amended with 1% ^{14}C -cellulose, ^{14}C -protein, or ^{14}C -starch and either 1, 10, or 100 ppm CGA-64250. The sample flasks were connected to an air manifold which terminated in NaOH traps to collect $^{14}\text{CO}_2$ to measure degradation of the labelled substrates.

Results

Over a 28 day period, CGA-64250 at levels, of up to 100 ppm had no statistically measurable effect on the degradation of cellulose, protein, or starch by soil microorganisms.

Conclusions

This study satisfies environmental chemistry requirements for data on the effects of pesticides on the function of soil microbes and shows that CGA-64250 does not inhibit the degradation of cellulose, starch or protein in soil.

"CGA-64250 Activated Sludge Metabolism" W. Spare, Biospherics Inc. Rockville Maryland, 8/8/80, Accession No. 244269.

Experimental Procedures

A domestic activated sludge (1.3g solid/liter), synthetic sewage, and ^{14}C -CGA-64250 were added in a model activated sludge system. The system was aerated for 23 hours at 23°C per cycle after which the solids were allowed to settle; supernatant fluid was drawn off for analysis, and fresh synthetic sewage and ^{14}C -CGA-64250 was added. The concentration of CGA-64250 was started at 0.1 ppm and increased daily for five days to 100 ppm. A control was also run. Bacteria, actinomycetes, and yeasts were quantified by plate counts, and protozoa by microscopy. Chemical analyses were by scintillation counting and TLC.

Results

CGA-64250 had no clearly discernible effect on the microbial population of the sludge relative to the controls. The ^{14}C recovery through the study was 97.2% with 86% in the liquid and the remainder in the solids. Less than 0.1% of the ^{14}C dose was trapped as volatile material. TLC analyses of the supernatant fractions demonstrated no degradation of the CGA-64250.

Conclusions

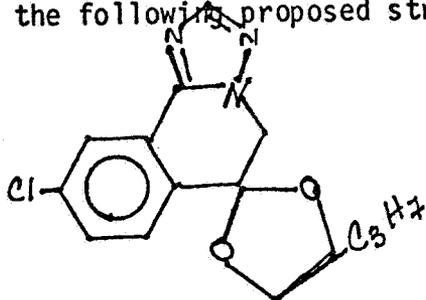
This is a valid study which satisfies environmental chemistry requirements for activated sludge metabolism data. The study demonstrates that CGA-64250 will have little effect on the function of an activated sludge unit but also that such units will not digest CGA-64250 effluent discharges.

"Photochemistry of CGA-64250; G.CC Miller, University of Nevada, Reno, Accession No 244269.

Experimental Procedures

Ten ppm solutions of CGA-64250 were prepared in distilled water or 1% acetone sensitizer in distilled water and exposed to mercury arc UV (9313 nm) or natural sunlight on 7/16/80. Analysis was by reverse-phase HPLC.

The half-life of CGA-64250 loss in mercury arc lamp was 53 hours in distilled water and 2.5-3.5 hours in the sensitized acetone solutions. Under natural sunlight, roughly one-half of the starting material remained at the end of twelve days in distilled water, whereas a half-life of less than a day was seen in the 1% acetone solutions. One major metabolite was noted by HPLC, with the following proposed structure:



Conclusions

This study satisfies environmental chemistry data requirements for aqueous photodegradation and demonstrates that CGA-64250 degrades rapidly in solution with photosensitizers.

- 2.9 Bioconcentration of CGA-64250, reported in part on 9-20-80 by EG and G Bionomics, Wareham, Mass. Accession No. 244269

This study will not be reviewed for validity because no experimental details have been provided. The attached data Tables 14 and 15 indicate that CGA-64250 is accumulated only to a low extent after 28 days of exposure (33 x in edible tissue, 227 x in non-edible tissue, 94.1 x in whole fish).

TILT CGA-64250 Reviews

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3.0 Executive Summary

CIBA-GEIGY has submitted the following acceptable data for registration of technical CGA-64250 and TILT 3.6E.

- a. Hydrolysis-CGA-64250 is stable towards hydrolysis at pH 1-13.
- b. Soil photolysis-CGA-64250 did not photodegrade over 24 hours on a soil surface.
- c. Adsorption/desorption-CGA-64250 adsorbed extensively to soils (K_D ranged from 8.5 to 59.0)
- d. Effects of Pesticide on Soil Microbes-CGA-64250 did not significantly affect soil respiration and nitrification-probably through a general phytotoxic action. Degradation of cellulose, starch, and protein were not affected.
- e. Soil mobility-CGA-64250 leached moderately through sandy soil with low organic matter, as did aged residues.
- f. Aerobic/Anaerobic Soil Degradation-CGA-64250 degraded slowly in aerobic soil (half-life = 10 weeks) but not in anaerobic on sterile soils.
- g. Aqueous photolysis - CGA-64250 photodegraded rapidly in natural or simulated sunlight in the presence of photosensitizers (half-life 2.5-24 hours), but less rapidly without sensitizers.
- h. Fish Accumulation - the status of the study is incomplete pending submission of a complete data package for validation.
- i. Activated sludge metabolism - The submitted study shows that CGA-64250 has little measureable effect on the function of the activated sludge process, nor is the sludge process effective in destroying CGA-64250.

4.0 Recommendations

1. CIBA-GEIGY has provided acceptable data to support the registration of technical CGA-64250 (hydrolysis, activated sludge).
2. EFB anticipates no significant problems arising from the environmental properties of CGA-64250 for the proposed turf use, based on the submitted data. However, EFB notes that CGA-64250 may leach in sandy, low organic matter soils, and suggests that future requests for major use registrations be deferred to TOX branch for a complete assessment of hazard.
3. EFB notes that the data package for the proposed use is incomplete. The following course of action is requested by EFB:

- a. Submit the complete fish accumulation study for review and validation.
- b. An out door field dissipation study is lacking. In lieu of this, the soil dissipation half-life of 10 weeks is taken as reflecting the field dissipation. In other words, this is a persistent chemical which may build up on repeated application. EFB defers to EEB to judge the potential significance of this. EFB also states that a valid field dissipation study is an absolute requirement for any future major uses on food crops.
- c. No rotational crop data were provided. A rotational crop restriction on the label is in order, therefore.

Willie Garner
Henry Appleton *for*
Chemist
Section 1, EFB/HED

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