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21 OCT 1983

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Date Out EFB: 21 OCT 1983

TO: H. Jacoby
Product Manager 21
TS-767

FROM: Dr. Richard Moraski
Acting Chief
Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division

R. Moraski

Attached please find the environmental fate review of:

Reg./File No.: 100-AUR

Chemical: CGA-64250

Type Product: Fungicide

Product Name: Banner

Company Name: CIBA-Geigy

Submission Purpose: Submission in response to previous review

New chemical on turf

ZBB Code: Other

ACTION CODE: 176

Date in: 8/19/83

EFB # 3500

Date Completed: 10/18/83

TAIS (level II) Days

61 7

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

1.0 INTRODUCTION

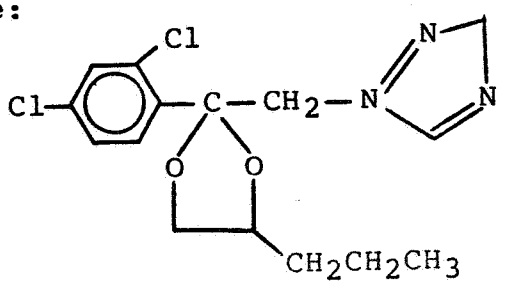
CIBA-Geigy has submitted a response to previous EAB review of their application for registration of the Banner R (CGA-64250, as a. i.) for use as a fungicide on turf.

1.1 Chemical

Chemical code name: CGA-64250

Chemical name: 1-(2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl)methyl)-1H-1,2,4-triazole

Chemical structure:



2.0 DIRECTIONS FOR USE

The revised use directions are appended to this review. In summary, the rate of application has been lowered from 4 oz/1,000 square feet (1.5 lb. a. i./A) to 1.0 oz/1,000 square feet (0.375 lb. a. i./A). Repeat applications are proposed at 14 - 21 day intervals.

3.0 DISCUSSION OF DATA

All studies in this review are included in the submission with Accession No. 250783.

This discussion lists EAB original conclusion, the CIBA-Geigy reply, followed by the EAB response:

3.1 EAB conclusion: This use involves a significantly higher application rate than the previous registration for use on grass grown for seed (1.5 lb. a. i./A vs 0.225 lb. a. i./A). The field dissipation data requirement has still not been satisfied. The registrant should submit the requisite field dissipation study at the higher proposed application rate.

3.2 CIBA-Geigy reply: Due to phytotoxicity concerns on certain turf grasses, CIBA-Geigy is now lowering the rate of application to one-fourth of that previously proposed, or 0.375 lb. a. i./A.

Also, Soil dissipation data are enclosed for CGA 64250 applied at up to 4 lb. a. i. per acre.

3.3 EAB notes the revised directions for use. The additional data are reviewed:

3.3.1 The Uptake of Triazole-^{14}C-CGA 64250 and Its Soil Degradation Products in Field Rotational Winter Wheat, Lettuce, Corn, and Carrots. May 20, 1982. J. Staley, et al. CIBA-Geigy Report ABR-82007. Reference 6.

Note: Only the soil dissipation portion of the study will be reviewed here. Crop data will be summarized.

Procedure

A Mississippi field plot of silt loam soil (38.5% sand, 49.6% silt, 11.9% clay, 1.71% organic matter, pH 7.05, CEC= 15.1 meq/100 g) planted in peanuts was treated with eight multiple sprays at a rate of 70 g ai/A (0.154 lb. ai) foliar spray and two ground applications at rate of 0.375 lb ai/A of ^{14}C-CGA 64250 (Total application of 2 lb ai/A). After the mature peanuts were harvested (21 weeks later) soil was tilled and winter wheat was planted. Other rotational crops (lettuce, carrots, and corn) were planted in the following spring.

During the period soil samples were taken at 0-6, 6-12 and 12-16 inch soil depths. Soil samples were extracted with methanol/water solution (90/10) and/or combusted according to procedures referenced but not submitted (AG-351, -223, -252).

Results

The authors report that, after the 8 foliar applications and 2 ground applications, the soil contained 0.19 ppm and 1.52 ppm CGA-64250 equivalents, respectively. After 21 weeks, the soil level had dropped to 0.89 ppm CGA 64250 equivalents. After 62 weeks, 0.49 ppm CGA-64250 equivalents were found in the 0-3 inch soil depth. ^{14}C residues were found in the 3-6 inch and 6-9 inch soil depths at 0.13 ppm and 0.09 ppm CGA-64250 equivalents, respectively. Over the test period, extractable organic material declined while the amount of non-extractable (bound) material increased. See Table 1.

Control samples contained non-detectable (< 0.05 ppm) levels CGA 64250.

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The authors referenced a report (not submitted) reporting that TLC characterization of organo-soluble residues indicated that 5 weeks after initial application the parent material accounted for 46% of the applied ^{14}C in the 0-3 inch soil core. By 21 weeks, 32% in this layer was unchanged parent. After 52 weeks, parent accounted for 16% of the total ^{14}C and non-extractable accounted for 67%. [Note: Table 3 of the study (Table 1 of this review) show that 32% (of 46.5% of the total ^{14}C) and not 46% of the organo-soluble fraction was parent CGA 64250. Data for the 21 week interval are not presented in this table.]

The registrant, referring to this study in the Reference "Summary" reported a half-life of 306 days of total ^{14}C from ^{14}C-triazole-CGA 64250 treated field soil.

Note: The authors report that at maturity, winter wheat contained 1.66 to 7.39 ppm; corn 1.33 to 13.18 ppm; and lettuce, carrot stalks and roots contained 1.30 to 7.35 ppm ^{14}C-CGA-64250 equivalents. Analysis of the radio-activity indicted that the residues were plant conjugates of the parent compound and the triazole moiety of the soil degradation products.

Conclusion

CGA 64250 degraded slowly in Mississippi silt loam soil with a calculated half-life of >300 days.

The data indicate also that CGA-64250 residues may leach to the 6-9 inch soil depth. Soil binding appears to be a major means of field dissipation.

Data on CGA 64250 soil degradation products were not presented.

Residues bound to soil may be available for rotational crop uptake.

Note: Rotational crops, when planted from 21 or 42 weeks after initial application contained measurable amounts of ^{14}C as the triazole moiety conjugated to plant constitutents

3.4 A series of large scale field dissipation studies were submitted:

3.4.1 AGA 5918 I-VII. Second Report. Field Test Number 3-FR-4-80 Project number 411924 B. Reference 10.

Peanuts growing in a Mississipp silt/clay loam soil (30% sand, 38% silt, 32% clay, 1.0-1.3% organic matter (two determinations), pH 7.1-7.3 (two determinations), CEC= 10.5 meq/100 g) were treated with two banded applications of CGA 64250 2.5G at 0.375 or 0.75 lb ai/A and eight foliar applications of CGA-64250 3.6E at 1.55 or 0.309 lb ai/A or 8 foliar applications of CGA 64250 3.6E at 1.55 lb ai/A. Total amount applied was 2 lb ai/A (1X) or 4 lb ai/A (2X).

Soil was sampled at intervals during the application period and continued to end of test, 315 days later. Soil cores were taken at 0-6, 6-12, and 12-18 inch soil depths.

For analysis of parent CGA 64250, soil was refluxed with methanol/water solution (90/10), cleaned up and quantitated by GLC.

Analysis of total CGA 64250 was by digestion of soil residues to dichlorobenzoic acid (DCBA) by reflux with nitric acid, water and table sugar. Quantitation was by GLC.

Results

Recoveries of 0.05 to 0.5 ppm fortification levels ranged from 77% to 135% for parent and from 55% to 111% for total (DCBA) CGA 64240.

Residues of parent and total CGA 64250 fluctuated (as expected, increasing immediately after application then decreasing) during the application period (0-14 days) and then slowly declined over the 16 to 315 day test period. See Table 2.

Detectable residues (>0.05 ppm) of parent CGA 64250 or total (DCBA) CGA 64250 not found in the 6-12 inch or 12-18 soil depth.

The registrant, refering to this study in the Reference "Summary," and using regression analysis calculates the first order half-life of 152 days (r^2= 0.8) and 206 days (r^2 = 0.73) for CGA 64250 parent residues and total (DCBA) 64250 residues, respectively, for the 2 lb ai/A application rate. Decline of the 4X rate did not appear to follow first order kinetics.

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Conclusion

CGA 64250 residues declined slowly under field conditions in a Mississippi silt/clay loam soil. The calculated half-life was 152 days when applied at 2 lb ai/A rate.

EAB notes that the samples were stored for an extended length of time before analysis. Storage stability data are not avialibale to show that CGA 64250 did not degrade over the period the soil was stored frozen.

Also, data on soil degradation products were not submitted. Rainfall and climatic data were not submitted in the study. This information is needed to complete this study.

3.4.2 AG A 6213 I-II Second Report. Field Test Number SW-FR-503-80. Project Number 411924B. Reference 11.

Peanuts growing in a Texas sandy loam soil (64.4% sand, 24.8% silt, 10.8% clay, 0.6% organic matter, pH 7.2, CEC=4.3 meg/100g) were treated with CGA 64250 in treatments as described in 3.4.1, above. Total application was 2.0 or 4.0 lb ai/A.

Irrigation water and rainfall approximated 19 inches during the application period. Data for the remainder of the test period were not submitted.

Soil samples were taken and extracted was described above. Soil was analyzed for parent residues by GLC.

Results

Recoveries were reported to range from 81% to 97% over the 0.05 to 0.2 ppm fortification levels.

Levels of CGA 64250 fluctuated during the application period (as expected) then slowly declined during the 248 day test period. Residues were found in the 0-6 inch soil depth 248 days after initial application. See Table 3.

No detectable residues of parent CGA 64250 were found below the 0-6 inch soil depth except in the 45 day sample of the 4X application rate. There 0.06 ppm residues were found.

The registrant, referring to this study in the Reference "Summary," using regression analysis calculated the first order half-life of CGA 64250 from application of 2 and 4 lb ai/A as 96 days (r^2 = 0.88) and 170 days (r^2 = 0.98), respectively, in the Texas sandy loam soil.

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Conclusion

CGA 64250 residues declined slowly under field conditions in the Texas sandy loam soil with a calculated half-life of 96 and 170 days after application of 2 and 4 lb ai/A. However, storage stability data are not available to show that CGA 64250 did not degrade during the period the soil was in frozen storage.

Analyses of soil degradation products were not submitted.

Irrigation and rainfall data were not submitted for the entire test period.

3.4.3 AG A 6213 I-II Third Report. Field Test Number SW-FR-503-80. Project Number 411924B. Reference 12.

This report continues the study described in 3.3.2, above. Data are presented for levels of total CGA 64250 (DCBA). However, samples were taken at day 0 (at eight foliar application), 199 and 248 days later. See Table 4.

The registrant, referring to this study, in the Reference "Summary," calculated the first order half life of 173 days (r^2 =0.97) and 196 days (r^2 = 0.96) for total (DCBA) CGA 64250 applied at the 2 lb ai/A (1X) and 4 lb ai/A (2X) rates, respectively.

Conclusion

EAB concludes that, while the samples are too few in number to adequately evaluate the decline of total CGA 64250 residues, the data indicate that residues were found in the 12-18 inch soil depths 248 days after last application.

3.4.4 AG-A 5999 I-IV Second Report. Field Test Number SE-FR-307-80. Project Number 411924 B. Reference 13.

Peanuts growing in a Georgia loamy sand (84% sand, 11.2% silt, 4.8% clay, 0.5% organic matter, pH= 6.7, CEC= 4.1 meq/100 g) were treated with CGA 64250 according to the treatments described in 3.4.1, above. A total of 2 or 4 lb ai/A was applied.

Soil was taken, extracted and quantitated as described earlier in 3.4.1, above.

Results.

Residue levels fluctuated (as expected) during the application period then slowly declined over the 260 day test period.

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Residues of parent CGA 64250 were found in the 0-6 inch soil depth 260 days after initial application. See Table 5.

No residues were found below the 0-6 inch soil depth except 0.06 ppm found in the 71 day sample of the 2 lb ai/A application.

The registrant, referring to this study in the Reference "Summary," and using regression analysis, calculated the first order half-life as 107 days (r^2=0.84) and 104 days (r^2= 0.99) for the 2 lb ai/A and 4 lb ai/A application rates, respectively. For the 8 foliar applications alone, the half-life was calculated to be 165 days (r^2= 0.90).

Conclusion

CGA 64250 residues declined slowly under field conditions in a Georgia sandy loam soil with a calculated half-life of 104 to 107 days. However, storage stability data were not submitted to show that the residues are stable over the period of time the soil was frozen before analysis.

Analysis of soil degradation products were not sumbmitted.

Also, rainfall and other climatic data were not submitted.

3.4.5 AG-A 5999 I-IV Third Report. Field Test Number SE-FR-307-80. Project Number 411924B. Reference 14.

This report is a continuation of that reviewed in 3.4.4, above. Data are presented on the analyses of total CGA 64250 (DCBA) in the Georgia loamy sand soil.

Soil was sampled at day 0 (after eight foliar application), and 71 days and 260 days later.

Results

Data are presented which show decline in total CGA 64250 (DCBA) residues. See Table 6.

The registrant calculates the half-life of total CGA 64250 (DCBA) as 200 days (r^2= 0.73) and 116 days (r^2=0.96) for the 2 lb ai/A and 4 lb ai/A treatments, respectivley. The half-life after the eight foliar applications is calculated as 457 days (r^2= 0.83).

Conclusion

While EAB concludes that too few samples were taken to adequately define total CGA 64250 (DCBA) decline in the

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Georgia loamy sand soil, the data indicate that after 71 days residues were found in the 6-12 inch soil depth. However, no residues were detected in the 260 day soil sample.

3.5 CIBA-Geigy submitted the field dissipation study entitled: "Distribution and Degradation of CGA 64250 (Tilt ^{R}) in a Field Soil." March 24, 1981. A. Keller. Project Report 10/81. Reference 4.

This study was conducted in a test plot within a field of Swiss soil. CGA 64250 degraded in the soil over the 13 month test period. After 60 days, 24% of the applied ^{14}C remained as unchanged parent material. Soil bound material steadily increased over the test period. One metabolite, CGA 118245, was identified which formed and then declined during the test period.

The author proposed that CGA 64250 degraded through hydroxylation of the dioxolane alkyl-side chain resulting in a unidentified compound containing the triazole moiety.

Conclusion

EAB considers this study as ancillary data since the Environmental Fate Guidelines require that field studies be conducted in the U. S.

3.6 CIBA-Geigy submitted the folowing laboratory aerobiic soil metabolism studies:

3.6.1 Degradation of CGA 64 250 (Tilt)^{R} in Soil Under Aerobic, Aerobic/Anaerobic and Sterile/Aerobic Conditions. Project Report 22/80. June 24, 1980. A. Keller. Reference 3.

This study was reviewed previously by EAB in review dated 6/17/81. It was accepted as satisfying the data requirement for the aerobic (and anaerobic) soil metabolism studies.

In the Swiss soil, the half-life of CGA 64250 was about 10 weeks under aerobic conditions. (Note: The half-life under anaerobic conditions was reported as > 12 weeks). Most of the material was bound to the soil particles. The metabolite, U_3, (1-[2-(2',4'-dichlorophenyl)-4-propanolyl-1,3-dioxolan-2-yl-methyl]-1H-1,2,4-triazole, CGA 118245) accounted for 23.6% of the ^{14}C after 52 weeks incubation

The metabolite, U_1, was not identified.

3.6.2 Degradation of CGA 64250 in Aerobic soil (provisional). Project Report 29/79. August 27, 1979. A. Keller. Reference 2.

This study is a preliminary report of that study listed in 3.5.1, above.

3.6.3 Degradation of ^{14}C-Dioxolane- and ^{14}C-Phenyl-Ring Labelled CGA 64 250 (Tilt ^{R}) in Aerobic Soil. Project Report 08/82. April 8, 1982. A. Keller. Reference 5.

This study provides additional information on the aerobic soil metabolism of CGA 64250.

In summary: In a Swiss silt loam soil, CGA 64250 degraded with a calculated half-life of 43-47 days. Degradation of the dioxolane and phenyl ring to CO_2 and soil binding were the major routes of dissipation under aerobic conditions.

The metabolite, CGA 136735 (1-[2-(2',4'-dichlorophenyl)-4-propan-1-ol-1-yl-1,3-dioxolane-2-yl-methyl]-1H-1,2,4-triazole), in equal amounts with CGA 118 245, were found as intermediates in the degradation of CGA 64250. A third intermediate found was postulated as probably being one hydroxylated at the 4- or 5-position of the dioxolane ring.

Note: The other major metabolite, U_1, found but not identified in the study reviewed and acepted by EAB (see 3.5.1 above) was not detected in this study using the dioxolane or phenyl ring labeled CGA 64250.

3.6.4 Degradation of CGA 64250 (Tilt ^{R}) in Aerobic Soil. Isolation and Identification of the Major, Polar Soil Metabolite. Project 45/82 (Addendum to Project 45/82). September 15, 1982. A. Keller. Reference 7.

This study provides additional information on the aerobic soil study reviewed and accepted by EAB previously.

In summary, the then unidentified metabolite, designated U_1, in the aerobic soil metabolism study (see 3.5.1, above) is now identified as 1,2,4-triazole.

3.6.5 Degradation of the Fungicide CGA 64250 in Two German Standard Soils Under Laboratory Conditions (provisional). Project Report 31/79. REF AG 2.52 AK/rr. Rference 2.

This study is considered ancillary. Data are presented that show the half-life of CGA 64250 in the Neuhofen and Hatzenbuhl German soils is greater than 16 weeks (end of study). No metabolites were identified.

3.7 Summary

From these studies submitted on aerobic soil metabolism the registrant has proposed a soil degradation scheme for CGA 64250. Degradation of CGA 64250 occurs through the hydroxylation of the n-propyl substituent in the dioxolane ring and mineralization (to CO_2) of the phenyl and dioxolane ring systems. This leaves the 1,2,4-triazole moiety of CGA 64250 which EAB considers as the residue of concern in the soil environment. See Figure 1.

3.8 CIBA-Geigy submitted the reports on methods for analysis of CGA 64250.

3.8.1 Gas Chromatographic Determination of CGA 64250 Residues in Crops. Method Number AG-354. Reference 8.

This report describes an analytical method in which plant samples are blended with 20% water/methanol for 10 minutes. The extract is then partitioned with dichloromethane and cleaned up by column chromatography. Final determination is by GLC using alkali flame ionization detector in the nitrogen-specific mode. The detection limit is reported as 0.05 ppm.

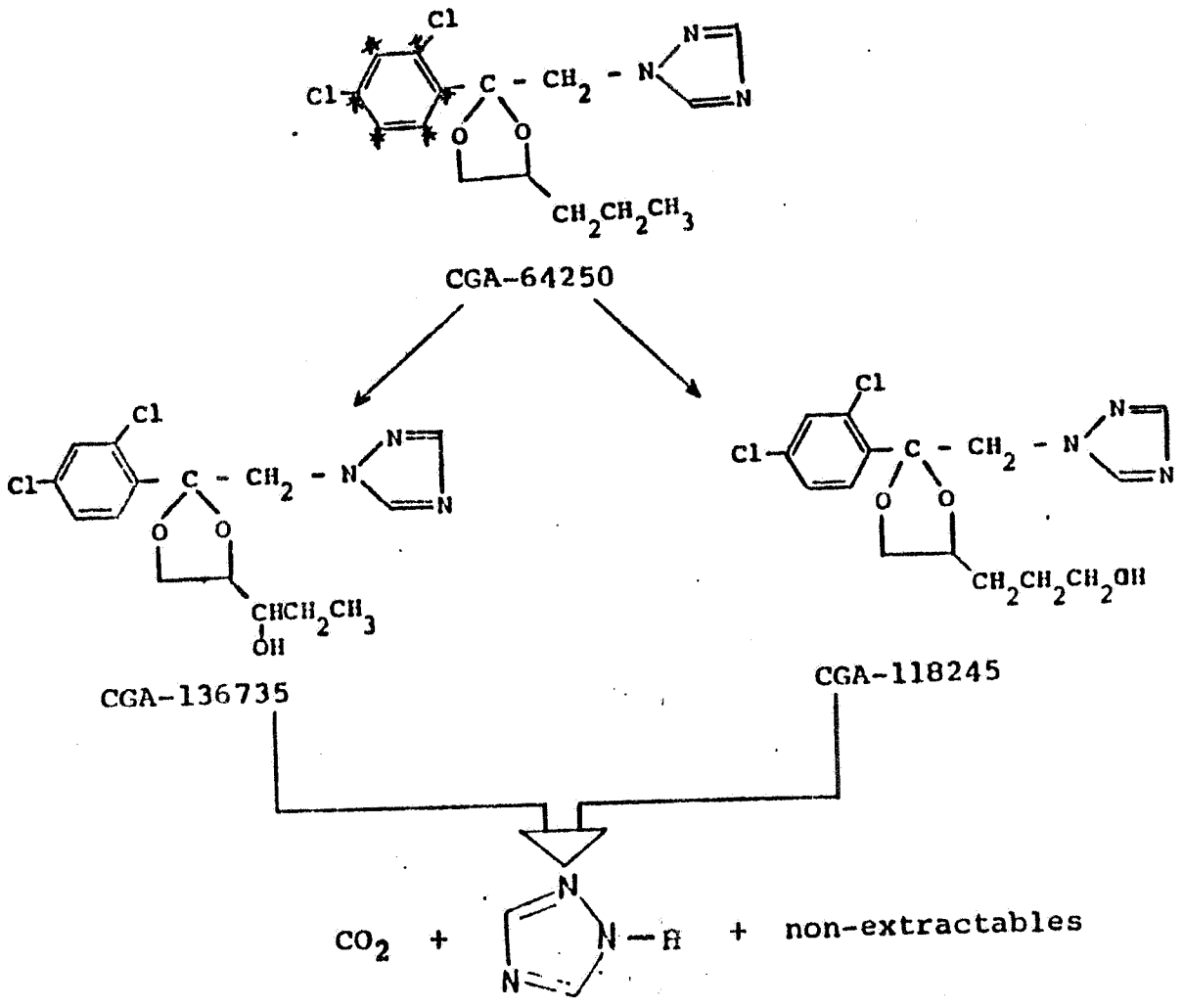
Note: It is not apparent to this reviewer which studies submitted used this analytical method.

3.8.2 Determination of Total CGA 64250 in Crops by Conversion to 2,4-Dichlorobenzoic Acid and Analysis by Gas Chromatography-Mass Spectrometry. Method Number AG-356. Reference 9.

Under reflux with 12N nitric acid, parent and metabolites of CGA 64250 are converted to 2,4-dichlorobenzoic acid. The extract is partitioned with dichloromethane and derivatized with diazomethane. The derivative is cleaned up using column chromatography. The cleaned extract is analyzed by gas chromatography-mass spectrometry in the chemical ionization mode. The limit of detection is 0.10 ppm expressed as CGA 64250 equivalents.

Note: This method modified for soil was used in the analyses for total (DCBA) CGA 64250 in the reviewed field dissipation studies.

FIGURE 1 : SOIL METABOLISM OF CGA-64250



1,2,4-H-Triazole
CGA-71019

4.0 EXECUTIVE SUMMARY

4.1 The registrant has lowered the application rate to 1 oz. per 1,000 square feet from the originally proposed 4 oz. per 1,000 square feet.

4.2 The registrant has submitted field dissipation data for CGA 64250 dissipation in agricultural soils resulting from application of 2 and 4 lb ai/A. In these studies, peanuts were the target crops. Results of these studies can be extrapolated to turf soils. The data show that CGA 64250 will degrade in various soils with a half-life ranging from 96 to 306 days. However, these studies lack certain information required by the Environmental Fate Guidelines:

- Rainfall and climatic data were not submitted for the duration of the individual tests.
- Formation and decline of degradation products were not analyzed and/or reported.
- Storage stability data for a time period equivalent to the length of time soil samples were frozen before analysis.

These deficiencies need to be resolved. However, based on the available data EAB can still conclude that CGA 64250 degradation products may be persistent and build up in the soil environment from repeated application to turf soil.

4.3 While formation and decline of degradation products were not reported in the field dissipation studies, EAB concludes that the the laboratory soil metabolism studies adequately define the degradation products of CGA 64250.

Based on the ^{14}C-triazole labeled CGA-64250 study, residues of the triazole moiety, namely 1,2,4-triazole, will be the residue of concern in the soil. Data from studies of ^{14}C-phenyl and ^{14}C-dioxolane labeled CGA 64250 indicate that these moieties are mineralized in soil to CO_2. This is expected to occur also in field soils. It appears that soil binding of the triazole moiety would be the major means of dissipation in the field.

It should be noted however, that these laboratory studies were conducted using Swiss soils. Soils from foreign sources

may be used to satisfy laboratory metabolism studies provided the soils have the same characteristics as soils in the U. S. The registrant has submitted all the requireed data on the similarities except the ratio to soil bacteria to soil fungi to soil actinomycetes.

Note: This reviewer is not aware if data on these ratios were submitted with the previous soil metabolism study reviewed and accepted by EAB. This information was not included with the currently submitted studies.

4.4 Residues of ^{14}C degradation productsd and total (DCBA) CGA 64250 were found in the field soils at 6-12 and 12-18 inch soil depths in some soils.

5.0 RECOMMENDATION

5.1 EAB can recommend for conditional registration of CGA 64250 for the proposed use on turf provided the registrant resolves certain deficiences in the submitted studies within a a reasonable length of time. These deficiencies include:

1. Rainfall and climatic data for the duration of the field dissipation studies.

2. Storage stability data for a length of time equivalent to the time period that the soil samples were frozen before extraction and then before analysis.

3. Data on the ratio of soil bacteria to soil fungi to soil actinomycetes for the Swiss soils used in the laboratory metabolism studies. This information is necessary to show that the Swiss soils used have the same microbial characteristics as The soils in the U. S.

5.2 EAB recommends that the registrant conduct a turf field dissipation study to monitor field leaching of CGA 64250 residues. Data presented in the submitted field dissipation studies show that, in some soils, residues were found in the 12 to 18 inch soil depth even though laboratory studies indicated a low potential for leaching of aged residues.

5.3 The registrant should be informed that, if future agricultural uses of CGA 64250 are proposed, a field study monitoring formation, decline and leaching of degradation products, including the metabolite, 1,2,4-triazole will be required. The soil in this study should be monitored to a sufficient depth to define leaching of soil degradation products, including 1,2,4-triazole.

Clinton Fletcher
Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division

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