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Shaughnessey No. 059101

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To: J. Ellenberger
Product Manager 12
Registration Division (TS-767)

From: Samuel Creeger, Chief
Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division (TS-769)

Attached please find the environmental fate review of:

Reg./File No: 44-448, -523 and -552

Chemical: Chlorpyrifos

Type Product: Insecticide

Product Name: LORSBAN 4E, 15G and 50W

Company Name: Dow

Submission Purpose: Review soil photolysis study in support of previous request for use on various crops

ZBB Code: _____

ACTION CODE: 305

Date in: 9/7/84

EFB # 4564-66

Date completed: 11/14/84

Tais (level II)	Days
62	2.0

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

1.0 INTRODUCTION

Dow Chemical Company is requesting ammended registrations for the use of chlorpyrifos (O,O-Diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate) on tobacco, tomatoes, sorghum, citrus fruits (tank mix with Spray Oils), corn, cherries, figs, cranberries, alfalfa, grapes, soybeans, onions and peanuts. These amendments had been previously rejected by EAB because of a soil photolysis data gap for chlorpyrifos. The subsequently submitted soil photolysis data were found to be deficient (EAB review of 2/2/84). A new soil photolysis study has been submitted with this request.

2.0 DISCUSSION OF DATA

2.1 Photodegradation of Chlorpyrifos on Commerce Soil Surface. Yackovich, P.R. and Miller, J.H. Agrichemical Products Department, Dow Chemical. July 27, 1984. Acc. No. 254395.

Procedure:

Commerce soil (36% sand, 50% silt, 14% clay, 0.6% OC), a loam soil, was slurried with distilled water, plated onto 9 cm round glass plates and amended with ^{14}C-chlorpyrifos. The plates were placed in a water jacketed glass chamber, covered with a glass plate and irradiated with light from a mercury arc lamp. (See Figures 1 and 4 on page 4.) The source air passed over Drierite to remove moisture and a bed of Ascarite TM to remove CO_2 before passing over the soil coated glass plates. Volatiles were trapped in a polyurethane foam plug and $^{14}CO_2$ was trapped in a bubbler trap containing Carbosorb. (See figure 3 on page 5.)

Replicate treated and dark samples were taken at days 1, 3, 6, and 12 days for liquid scintillation counting (TLC), extraction, and combustion analysis. The extracts were analyzed by High Performance Liquid Chromatography (HPLC).

Results:

The recovery of ^{14}C activity from the Commerce loam soil samples is summarized in Table 1 on page 6. Figures 5-8 on pages 7-10 give the amount of chlorpyrifos and its degradates found by HPLC in both treated and dark samples. Figures 9 and 10 on pages 11 and 12 graphically show the soil degradation of the parent and appearance of the photoproducts.

According to the registrant, chlorpyrifos did not follow first order kinetics. Instead, the data fit a non-linear regression analysis utilizing a two component model. This is shown in Figure 11 on page 13. The model assumes that the chemical resides in two soil compartments, one in which the chemical is available for degradation and another in which it is not. The kinetics are dependent on the degradation rate of the chemical in the available compartment and the transfer rate of the chemical between compartments. The plots of the computer generated analyses using the two compartment model is shown in Figures 12 and 13 on pages 14 and 15.

Conclusions:

Chlorpyrifos is rapidly degraded on soil both with light irradiation and without it. The degradation in both cases, however, is not linear. The initial rapid degradation begins to slow around day 3. About 40% of the parent is degraded by 2.2 days with light and 3.2 days without light. The major degradate is 3,5,6-trichloro-2-pyridinol in both light and dark. In the light, however, a minor degradation product, 2-methoxy-3,5,6-trichloropyridine, is also formed.

While this study indicates that under the test conditions light has little effect on the degradation of chlorpyrifos, it is not conclusive that the same effect would be evidenced in natural sunlight. The mercury arc lamp used does not emit all of the wavelengths which are present in natural sunlight. Further, a glass plate of unknown transmissibility was used to cover the reaction chamber containing the soil plates. Some of the wavelengths which were emitted could have been absorbed by the glass. The submission of the UV absorption spectrum of chlorpyrifos would help the reviewer evaluate whether the wavelengths absent from the artifical source but present in natural sunlight, would be absorbed by the pesticide and thus be possible cause of further photodegradation. The report does not state how the intensity of light of the artificial source relates to that of natural sunlight.

Several other concerns are also noted. The non-linear nature of the degradation of chlorpyrifos on soil is explained as a two compartment model with one compartment being available for degradation and one being unavailable for degradation. The only support for this assertion is that the model fits the data. No explanation as to the nature of the unavailability of chlorpyrifos is given. Does this represent binding to the soil, a conformational change, or what? Also, while the first half-life of chlorpyrifos is 3-5 days, what is the second half-life? How resistant or susceptible to photolysis is chlorpyrifos after the initial rapid degradation?

3.0 CONCLUSIONS

3.1 Under the test conditions chlorpyrifos degrades non-linearly with little difference in degradation between irradiated and unirradiated soil.

3.2 The major photoproduct is 3,5,6-trichloro-2-pyridinol with a minor photoproduct being 2-methoxy-3,5,6-trichloropyridine.

3.3 The relationship of the artificial light source to that of natural sunlight was not given. The kind of glass and the transmissibility of the glass covering the reaction chamber was not given.

3.4 This study does not satisfy the photolysis data requirement for chlorpyrifos.

3.5 We need to know if the "compartmentalized" behavior is unique to the single soil studied. Therefore, photolysis of chlorpyrifos on other soils should be studied.

4.0 RECOMMENDATION

In order for the reviewer to completely evaluate this study the registrant should submit information on the transmissibility of the glass plate used to cover the reaction chamber, the relationship of the artificial light intensity to that of natural sunlight, and the UV absorption of chlorpyrifos.

Further, to give some indication as to the nature of the non-linear degradation of chlorpyrifos, photolysis studies should be conducted on other soils. These studies should extend for the full 30 days to give a better indication of the photopersistance of chlorpyrifos after the initial rapid degradation. Soils from different but major chlorpyrifos use areas should be selected.

Norma Kay Whetzel
November 14, 1984
Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division

Page_____ is not included in this copy.

Pages 5 through 16 are not included.

The material not included contains the following type of information:

_____ Identity of product inert ingredients.

_____ Identity of product impurities.

_____ Description of the product manufacturing process.

_____ Description of quality control procedures.

_____ Identity of the source of product ingredients.

_____ Sales or other commercial/financial information.

_____ A draft product label.

_____ The product confidential statement of formula.

_____ Information about a pending registration action.

✓ FIFRA registration data.

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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.