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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

JUL 7 1986

MEMORANDUM

SUBJECT: PP#6E3389 (RCB No. 798). Chlorpyrifos on  
Leeks. Evaluation of Analytical Method  
and Residue Data (Accession No. 262136).

FROM: Nancy Dodd, Chemist *Nancy Dodd*  
Residue Chemistry Branch  
Hazard Evaluation Division (TS-769C)

THRU: Charles L. Trichilo, Ph.D., Chief *A. D. Schmitt per*  
Residue Chemistry Branch  
Hazard Evaluation Division (TS-769C)

TO: Hoyt Jamerson, PM 43  
Registration Support and Emergency  
Response Branch  
Registration Division (TS-767C)

and

Toxicology Branch  
Hazard Evaluation Division (TS-769C)

The petitioner, Interregional Research Project No. 4 (IR-4), on behalf of the IR-4 National Director, Dr. R.H. Kupelian and the Agricultural Experiment Stations of California and New Jersey request the establishment of a tolerance for the combined residues of the insecticide chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate] and its metabolite 3,5,6-trichloro-2-pyridinol (TCP) in or on the raw agricultural commodity leeks at 0.5 ppm (of which no more than 0.2 ppm is chlorpyrifos).

Tolerances for combined residues of chlorpyrifos and TCP have been established on a variety of commodities at levels ranging from 0.05 ppm on banana pulp, nectarines, peaches, pears, and plums (fresh prunes) to 25 ppm (food additive tolerance) on citrus oil (40 CFR 180.342; 21 CFR 123.85, 193.85, and 561.98).

Residue Chemistry Branch (RCB) has recommended (PP#3F2884/FAP#3H5396, K. Arne, January 24, 1984) for proposed revisions of several established tolerances in which the amount of chlorpyrifos per se is specified but the combined residue level of parent plus TCP would not change. Dow Chemical Company proposed the revisions to lower the effect of existing tolerances on the acceptable daily intake (ADI).

A Registration Standard for chlorpyrifos was completed on September 30, 1984.

A letter of authorization dated March 12, 1986 has been sent by Robert Bischoff of Dow Chemical Company to Hoyt Jamerson, RD, OPP, to authorize use of all relevant Dow data concerning chlorpyrifos in support of the IR-4 petition on leeks.

### Conclusions

1. At present, some plant metabolism data gaps need to be resolved (see RCB's memorandum of July 15, 1985 re: EPA Registration No. 464-523). However, if no detectable residues (i.e. residues above the sensitivity of the analytical methodology) are found in leeks as a result of this proposed use (see Residue Data section), RCB could conclude that the nature of the residue in leeks is adequately understood for the purpose of this petition only. The residues of concern would be chlorpyrifos and its metabolite TCP.
2. Adequate analytical methods are available for enforcement of the proposed tolerance on leeks.
3. Adequate storage stability data are available.
- 4a. On page 30 (Minor Use Residue Form) of Accession Number 262136, the New Jersey residue range found is stated to be < 0.2 to 1.4 ppm for TCP on "whole leek" although elsewhere residues of TCP are stated to be < 0.2 ppm. The petitioner should provide an explanation.
- 4b. Since residue data on leeks are submitted for only California and New Jersey, a tolerance with regional registration should be proposed or additional residue data for other geographic areas are needed.
- 4c. Plants are not to be trimmed before analysis. In California (see p. 49 of Accession Number 262136 - Minor Use Residue Form), field processing included peeling off of outer skins and removal of extreme tips. Therefore, additional residue data on the

untrimmed raw agricultural commodity are needed to support the proposed use in California, or use could be restricted to New Jersey.

- 4d. The Section B/label should be revised to indicate application in a minimum of 70 gallons of total drench per acre; this is reflective of the residue data submitted. As an alternative, the petitioner may submit additional residue data using a spray volume of 40 gallons (see Residue Data section).
- 4e. RCB reserves its conclusion concerning the adequacy of the proposed 0.5 ppm chlorpyrifos tolerance on leeks until Conclusions 1, 4a, 4b, 4c, and 4d above are resolved.
5. An International Residue Limits (IRL) Status sheet is attached. There are no Codex, Canadian, and Mexican tolerances for chlorpyrifos on leeks. Therefore, no compatibility questions exist with respect to Codex.

#### Recommendation

RCB recommends against the proposed use of chlorpyrifos on leeks for reasons given in conclusions 1, 4a, 4b, 4c, 4d, and 4e above.

If the proposed use is restricted to leeks grown in New Jersey and California only, any future tolerance for chlorpyrifos on leeks should be included in a separate subsection under 40 CFR 180.342 to avoid confusion regarding future 24(c) registrations and crop-grouping eligibility. The "tolerances with regional registration" would be referenced along with future regional registration tolerances in a new subsection (n) under 40 CFR 180.1 which would define the Agency's interpretation of "tolerances with regional registration." An appropriate interpretation for 40 CFR 180.1, subsection "n," would be:

Certain tolerances are based on geographically limited residue data. These "tolerances with regional registration" are included in separate subsections under 40 CFR 180.101 through 180.999. In order to expand the area of usage on these crops, additional residue data generated in these areas will be required. Persons seeking geographically broader registration on these crops should contact the appropriate EPA product manager concerning whether additional residue data are required.

## Detailed Considerations

### Manufacture and Formulation

The chlorpyrifos manufacturing process is described in Confidential Appendix A of the Registration Standard. Technical chlorpyrifos is at least 94 percent pure.

Product chemistry data gaps were cited in the Registration Standard (see Chlorpyrifos Registration Standard and Dow's response to product chemistry data gaps in S. Malak's memorandums dated September 11, 11, 25 and 27, 1985).

The formulation proposed for use on leeks is Lorsban® 4E Insecticide (EPA Registration No. 464-448). This formulation contains 40.7 percent active ingredient (4 lbs ai/gal). The composition of this formulation is discussed in RCB's review of PP#4F1445. All inerts in this formulation are cleared under 40 CFR 180.1001.

### Proposed Use

#### Leeks

Apply at planting as an in-furrow drench. Apply Lorsban 4E at the rate of 1.1 fluid ounces per 1000 linear feet of row at an 18-inch row spacing (1 lb ai/A). Use a minimum of 40 gallons of total drench per acre. Incorporate to a depth of 1 to 2 inches. Do not make more than one application per year.

RCB concludes that the Section B/label should be revised to indicate application in a minimum of 70 gallons of total drench per acre. This is reflective of the residue data submitted. As an alternative, the petitioner may submit additional residue data using a spray volume of 40 gallons (see Residue Data section).

### Nature of the Residue

#### Plants

The nature of the residue in plants has been discussed in RCB's review of FAP#1H5295 on tomato pomace (K. Arne, November 20, 1981) and in the Chlorpyrifos Registration Standard (September 30, 1984). To resolve legume, corn, and root crop metabolism data gaps cited in the Chlorpyrifos Registration Standard, Dow intends to conduct corn and sugar beet metabolism studies (see N. Dodd memorandum of July 15, 1985 re: EPA Registration No. 464-523).

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If no detectable residues are found in leeks as a result of this proposed use (see Residue Data section), RCB could conclude that the nature of the residue in leeks is adequately understood for the purpose of this petition only. The residues of concern would be chlorpyrifos and its metabolite TCP.

#### Analytical Methods

The analytical method used to determine residues of chlorpyrifos on leeks was "Determination of Residues of O,O-Diethyl-O-(3,5,6-Trichloro-2-Pyridyl) Phosphorothioate in Snapbeans and Snapbean Forage by Gas Chromatography," by R.L. McKellar, Dow Chemical Company, ACR 72.15, December 4, 1972. Samples are extracted with acetone. (Modification to published method: Follow extraction and filtration with Reynolds Methods.) The compound in hexane is cleaned up on a Florisil column. Residues are determined by gas chromatography using a flame photometric detector. Recoveries for leeks fortified at 0.1 and 0.5 ppm were 110 percent and 98 percent, respectively. The petitioner's residue data indicate that the sensitivity of the method for chlorpyrifos is ca. 0.05 ppm in the New Jersey study and ca. 0.01 ppm in the California study. This method was submitted by Dow Chemical Company in PP#4F1445 (Tab D.4). This method is similar but not identical to Method I in PAM II. EPA has conducted a method tryout on another method (Method II in PAM II) on peaches.

The analytical method used to determine combined residues of 3,5,6-trichloro-2-pyridinol and parent compound in leeks was "Determination of Residues of 3,5,6-Trichloro-2-Pyridinol in Lima and Snapbean Forage and Beans by Gas Chromatography," by R.L. McKellar, Dow Chemical, ACR 71.19R. Samples are heated with methanolic sodium hydroxide before extraction. (Modification to published procedure: The step of hydrolyzing chlorpyrifos to 3,5,6-trichloro-2-pyridinol (TCP) with concentrated HCl and NaCl is skipped.) The sample is partitioned with benzene, put through an acid alumina column, partitioned to sodium bicarbonate and then to benzene. Residues are determined by electron capture GLC. Recoveries for leeks fortified with TCP at 1.0 ppm were 91 to 100 percent. The claimed sensitivity of the method is 0.2 ppm. Method ACR 71.19R is Method VII in PAM II.

RCB concludes that adequate analytical methods are available for enforcement of the proposed tolerance on leeks.

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Residue DataStorage Stability

The storage stability of chlorpyrifos is discussed in the Chlorpyrifos Registration Standard. Various fruits, vegetables, and nuts were fortified at levels ranging from 0.1 to 1.0 ppm and stored at -18 °C (0 °F) for 5 to 27 months. Residues of chlorpyrifos or TCP ranged from 66 to 109 percent (average 85%) of the initial fortification levels. Residues in apples and walnuts stored 4 years were 61 to 105 percent and 82 to 100 percent, respectively, of the initial fortification levels. Residues of chlorpyrifos and TCP in tomatoes stored 29 months at -18 °C were 82 to 88 percent and 89 to 109 percent, respectively, of the initial fortification levels.

Samples of leeks were treated with 0.1 ppm chlorpyrifos on December 6, 1984 and stored at -10 °F. Samples were analyzed on May 21, 1985. Recoveries were 95 to 100 percent.

RCB concludes that adequate storage stability data are available.

Leeks

Two studies on leeks were conducted; one was in New Jersey and the other was in California.

In New Jersey, transplanted leeks were treated with Lorsban 4E at the rate of 1.1 fl oz/1000 linear feet of row (1.0 lb ai/A). The ground application was a drench with soil incorporation in 73 gallons water per acre. Mature plants were harvested 135 days after treatment. Samples were frozen at -20 °F to -10 °F between sampling and analysis. Samples were analyzed for chlorpyrifos and TCP at 9 and 10 months, respectively, after harvest. Residues in leeks were < 0.05 ppm chlorpyrifos and < 0.2 to 1.4 ppm TCP. Controls were < 0.05 ppm chlorpyrifos and < 0.2 ppm TCP.

In California, a preplant soil application and incorporation of chlorpyrifos was made with ground equipment at the rate of 1.83 fl oz/1000 linear feet with a 30" row spacing (1.0 lb ai/A). Application was made in 100 gal water/A. Leeks were seeded. Mature plants were harvested 127 days after treatment. Field processing included peeling off of outer skins and removal of extreme tips. Samples in California were frozen at -10 °F to -17.8 °C between sampling and analysis (2 months). Residues on leeks and controls were < 0.01 ppm chlorpyrifos and < 0.2 ppm TCP.

According to Considine's Foods and Food Production Encyclopedia, the leek "resembles the onion in its adaptability

and cultural requirements." According to R. Perfetti's memorandum "IR-4 Crop Grouping Comments" dated December 8, 1983, the ideal geographic representation for residue data would be Texas, California, Arizona/New Mexico for green onions and New York, Michigan, Oregon/Washington, Idaho, and Colorado for bulb onions. Since residue data on leeks are submitted for only California and New Jersey, a tolerance with regional registration should be proposed or additional residue data for other geographic areas would be needed.

RCB concludes the following:

1. On page 30 (Minor Use Residue Form) of Accession Number 262136, the New Jersey residue range found is stated to be < 0.2 to 1.4 ppm for TCP on "whole leek" although elsewhere residues of TCP are stated to be < 0.2 ppm. The petitioner should provide an explanation.
2. Since residue data on leeks are submitted for only California and New Jersey, a tolerance with regional registration should be proposed or additional residue data for other geographic areas are needed.
3. Plants are not to be trimmed before analysis. In California (see p. 49 of Accession Number 262136), field processing included peeling off of outer skins and removal of extreme tips. It is noticed on the "Minor Use Residue Form" that residues were reported as < 0.01 ppm. Therefore, additional residue data on the untrimmed raw agricultural commodity are needed to support the proposed use in California, or use could be restricted to New Jersey.
4. RCB reserves its conclusion concerning the adequacy of the proposed 0.5 ppm chlorpyrifos tolerance on leeks until #1, #2, and #3 above are resolved.

#### Meat, Milk, Poultry, and Eggs

No feed items are involved in this proposed use of chlorpyrifos on leeks. Therefore, RCB concludes that this use falls in category 3 of §180.6(a) with respect to residues in meat, milk, poultry, and eggs.

#### Other Considerations

An International Residue Limits (IRL) Status sheet is attached. There are no Codex, Canadian, or Mexican tolerances for chlorpyrifos on leeks. Therefore, no compatibility questions exist with respect to Codex.



Attachment 1: International Residue Limit Status sheet

cc: RF, Circu, Reviewer - N. Dodd, EAB, EEB, PP#6E3389, FDA,  
PMSD/ISB-Eldredge

RDI:J.H.Onley:6/17/86:R.D. Schmitt:6/17/86

TS-769C:RCB:CM#2:RM 810:X1681:N. Dodd:Kendrick & Co:7/3/86

INTERNATIONAL RESIDUE LIMIT STATUS

M. Gould

CHEMICAL Chlorpyrifos

PETITION NO GE3389

CCPR NO. 17

A. Jones  
6/10/88

Codex Status

Proposed U. S. Tolerances

No Codex Proposal  
Step 6 or above

Residue (if Step 9): \_\_\_\_\_

Residue: chlorpyrifos\* and its  
metabolite 3,5,6-trichloro-  
2-pyridinol

chlorpyrifos

Crop(s) Limit (mg/kg)

Crop(s) Tol. (ppm)

none (on leaves)\*\*

leeks 0.5 (of which no more  
than 0.2 ppm is  
chlorpyrifos)

CANADIAN LIMIT

MEXICAN TOLERANCIA

Residue: \_\_\_\_\_

Residue: \_\_\_\_\_

chlorpyrifos

chlorpyrifos

Crop Limit (ppm)

Crop Tolerancia (ppm)

none (on leaves)\*\*

none (on leaves)

Notes:

\* 0,0-diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate  
\*\* There is a 0.05 ppm Codex limit of determination limit on onions and the same for  
Canada at 0.0 ppm.