



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

PMSD / JSB
0289-D

AUG 14 1985

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#5F3271 (RCB#1198). Permethrin on Cherries and Plums. Evaluation of Analytical Methods and Residue Data. (Accession #073659).

FROM: Nancy Dodd, Chemist *Nancy Dodd*
Tolerance Petition Section II
Residue Chemistry Branch
Hazard Evaluation Division (TS-769)

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

TO: George LaRocca, Product Manager #15
Insecticide-Rodenticide Branch
Registration Division (TS-767)

and

Toxicology Branch
Hazard Evaluation Division (TS-769)

FMC Corporation requests the establishment of tolerances for combined residues of the insecticide permethrin [(3-phenoxyphenyl) methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] and its metabolites dichlorovinyl acid and m-phenoxybenzyl alcohol in or on the raw agricultural commodities cherries at 3.0 ppm and plums at 1.0 ppm.

Tolerances have been established for residues of permethrin and its metabolites 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (dichlorovinyl acid; DCVA), and (3-phenoxyphenyl) methanol (3-phenoxybenzyl alcohol; 3-PBA) on various raw agricultural commodities at levels ranging from 0.05 ppm to 60 ppm. Tolerances have been established for residues of permethrin and its metabolites DCVA, 3-PBA, and 3-phenoxybenzoic acid on animal commodities including meat, fat, and meat by-products of cattle, goats, hogs, horses, poultry, and sheep; eggs, and milk fat/whole milk at levels ranging from 0.05 to 3.75 ppm. A tolerance for permethrin per se is established on cottonseed at 0.05 ppm (40 CFR 180.378). There is no Registration Standard for permethrin at this time.

- 1a. A revised Section B should be submitted wherein the label contains both a restriction against grazing treated orchards and a restriction against cutting cover crops for feed.
- 1b. A revised Section B should be submitted wherein the label specifies a line of division such as "east of the Mississippi" and "west of the Mississippi" instead of "east" and "west." The terms "eastern" and "western" United States are too general.
- 2a. The nature of the residue in cherries and plums is adequately understood. At this time, the residues of concern in cherries and plums are permethrin and its metabolites 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (DCVA) and (3-phenoxyphenyl) methanol (3-PBA).
- 2b. The nature of the residue in animals is adequately understood. At this time, the residues of concern in animals are permethrin, DCVA, 3-PBA, and 3-phenoxybenzoic acid (3-PBAcid).
- 2c. RCB repeats the following statement:

"Some tolerances for synthetic pyrethroid compounds have been regulated in terms of parent compound or in some cases, parent and metabolites. In an attempt to determine whether there is sufficient information available to draw a conclusion on how these pyrethroids should be regulated, RCB is conducting a comparative study on the metabolism of different pyrethroids. This will enable RCB to provide TOX with information regarding the levels of pyrethroid metabolites on crops so that TOX will be able to make a decision on whether pyrethroids need to be regulated in terms of parent compound only, parent and metabolites, or whether additional metabolism data are needed on various crops. However, the tolerance expression for permethrin residues (parent plus metabolites) on raw agricultural commodities as stated in 40 CFR 180.378 is appropriate at this time. Any recommendations resulting from the preceding study will be considered at a later date."

3. Adequate analytical methods are available for enforcement of the proposed tolerances for permethrin and its metabolites DCVA and 3-PBA in cherries and plums.
4. Available storage stability data are adequate.
5. Residues resulting from the proposed use will not exceed the proposed tolerance of 3.0 ppm on cherries.
6. Residues resulting from the proposed use will not exceed the proposed tolerance of 1.0 ppm on plums.
7. Residue data for dried prunes processed from fresh fruit bearing residues at or near the proposed tolerance are needed. If there is a concentration of residues in dried prunes, then the petitioner will need to submit a proposal for an appropriate food additive tolerance.
8. No food or feed items are involved in this proposed use on cherries and plums. No secondary residues are expected to occur in meat, milk, poultry, or eggs as a result of the proposed use. Therefore, this use falls in category 3 of Section 180.6(a) with respect to residues in meat, milk, poultry, and eggs.
9. An International Residue Limit Status sheet is attached to this review. A Codex IRL has been proposed for permethrin on stone fruit at 2 mg/kg. A Canadian tolerance has been established for permethrin on plums at 0.5 ppm. No Mexican tolerances have been established for permethrin on plums or cherries. Thus, the Codex proposal and Canadian tolerance are not compatible with the proposed U.S. tolerances on cherries and plums with respect to the tolerance expression and tolerance levels. Concerning the residue level for plums, RCB would have no objection to raising the level from the proposed 1.0 ppm level to 2 ppm, if toxicologically feasible, in order to coincide with the Codex proposal of a 2 mg/kg level on stone fruit.

Recommendation

RCB recommends against the proposed tolerances for permethrin and its metabolites dichlorovinyl acid (DCVA) and m-phenoxybenzyl alcohol (3-PBA) on cherries at 3.0 ppm and on plums at 1.0 ppm for reasons given in conclusions 1a, 1b, and 7 above.

Detailed Considerations

Manufacture and Formulation

RCB refers to a previous review in which the manufacturing process for technical permethrin has been discussed (PP#8F2034, A. Rathman, March 13, 1978). The technical material is approximately 92 percent pure. Impurities in the technical material are not expected to cause a residue problem.

The formulation proposed for use on cherries and plums is FMC's Pounce® 3.2 EC Insecticide (EPA Registration No. 279-3014) which contains 38.4 percent active ingredient (3.2 lb ai/gal). All inert ingredients have been cleared under 40 CFR 180.1001.

Proposed Use

Cherries and Plums

Apply Pounce 3.2 EC to cherries and plums when insects appear or feeding is noticed. Apply by ground or aerial equipment at a rate of 1 to 2 oz Pounce 3.2 EC (0.025-0.05 lb ai) per 100 gal water, not exceeding 400 gal water/A. This is a maximum rate of 0.2 lb ai/A/application. In the Western United States, do not exceed four applications/season to cherries and plums, with no more than three applications after petal fall. In the Eastern United States, do not exceed six applications/season to cherries, with no more than four applications after petal fall. Do not exceed seven applications to plums in the Eastern United States, with no more than six applications after petal fall. Observe a 3-day PHI for cherries and plums. Rotational crops which are not on the label should not be planted within 60 days of the last application. Do not graze livestock in treated cherry and plum orchards.

RCB concludes that a revised Section B should be submitted wherein the label contains both a restriction against grazing treated orchards and a restriction against cutting cover crops for feed.

RCB also concludes that the revised Section B should be submitted wherein the label specifies a line of division, such as "east of the Mississippi" and "west of the Mississippi" instead of "east" and "west." The terms "eastern" and "western" United States are too general.

Nature of the Residue

Plants

No plant metabolism studies are submitted with this petition. RCB refers to previous reviews of metabolism of permethrin in apples, beans, cabbage, cotton, and tobacco (PP#7G1891, A. Rathman, March 10, 1977; PP#8G2029, A. Rathman, December 27, 1978; and PP#0F2389, J. Onley, April 10, 1981). The major metabolic pathway involves hydrolysis at the ester bond. The major metabolites are 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (dichlorovinyl acid; DCVA) and (3-phenoxyphenyl) methanol (3-phenoxybenzyl alcohol; 3-PBA).

RCB concludes that the nature of the residue in cherries and plums is adequately understood. At this time, the residues of concern in cherries and plums are permethrin and its metabolites 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DCVA) and (3-phenoxyphenyl)methanol (3-PBA).

Animals

No animal metabolism studies are submitted with this petition. RCB refers to previous reviews of metabolism of permethrin in chickens, dairy cattle, goats, and rats (PP#8F2034, A. Rathman, March 13, 1978; PP#8F2044, A. Rathman, April 24, 1978). Major metabolites in animals are DCVA, 3-PBA, and 3-phenoxybenzoic acid (3-PBAcid).

RCB concludes that the nature of the residue in animals is adequately understood. At this time, the residues of concern in animals are permethrin, DCVA, 3-PBA, and 3-phenoxybenzoic acid (3-PBAcid).

RCB reiterates the following statement from the review of PP#5E3225 (M. Firestone, Ph.D., June 4, 1985):

"Some tolerances for synthetic pyrethroid compounds have been regulated in terms of parent compound or in some cases, parent and metabolites. In an attempt to determine whether there is sufficient information available to draw a conclusion on how these pyrethroids should be regulated, RCB is conducting a comparative study on the metabolism of different pyrethroids. This will enable RCB to provide TOX with information regarding the levels of pyrethroid metabolites on crops so that TOX will be able to make a decision on whether pyrethroids need to be regulated in terms of parent compound only, parent and metabolites, or whether additional metabolism data are needed on various crops. However, the tolerance expression for permethrin residues (parent plus metabolites) on raw agricultural commodities as stated in 40 CFR 180.378 is appropriate at this time. Any recommendations resulting from the preceding study will be considered at a later date."

Analytical Method

Permethrin and its metabolites DCVA and 3-PBA are analyzed by three separate methods.

For analysis of permethrin in cherries and plums, blend the sample in 2:1 (v/v) hexane: 2-propanol. Filter. Add distilled water to the filtrate and shake. Collect the lower aqueous phase. Partition the residue from the lower aqueous phase into hexane. Clean up the residue on a Florisil column. Quantitate the residue by gas-liquid chromatography (GLC) using a ^{63}Ni electron capture detector. Recoveries of permethrin from cherries fortified at 0.1 to 1.0 ppm ranged from 80 to 94 percent. Recoveries of permethrin from plums and fresh prunes fortified at 0.1 to 0.3 ppm were 89 to 95 percent. Method sensitivity for permethrin in cherries and plums (fresh prunes) is 0.1 part per million.

For analysis of DCVA in cherries and plums, blend the sample with 2:1 (v/v) methanol:water. Filter. Adjust the pH of the filtrate to 8.3 with 10N sodium hydroxide and partition the residue into hexane. Then back-extract the residue from the hexane into 0.01 N sodium hydroxide. Subject the residue to acid hydrolysis using hydrochloric acid. After reverse-phase column cleanup, derivatize the residue with pentafluorobenzyl bromide. Clean up the residue on a Florisil column. Quantitate the residue on a capillary GLC using a mass selective detector. Recoveries of DCVA from cherries fortified at 0.05 or 0.10 ppm ranged from 60 to 106 percent. Recoveries of DCVA from plums and fresh prunes fortified at 0.05 ppm ranged from 76 to 106 percent. Method sensitivity for DCVA in cherries and plums (fresh prunes) is 0.05 ppm.

For analysis of 3-PBA (MPBA) in cherries and plums, follow the steps for analysis of DCVA through the reverse-phase column cleanup. Then derivatize the residue with heptafluorobutyric anhydride. Clean up the residue on a Florisil column. Quantitate the residue on a capillary GLC using a mass selective detector. Recoveries of 3-PBA from cherries fortified at 0.05, 0.10, or 0.20 ppm were 60 to 118 percent. Recoveries of 3-PBA from plums and fresh prunes fortified at 0.05 to 0.10 ppm were 74 to 112 percent. Method sensitivity is 0.05 ppm for 3-PBA in cherries and plums (fresh prunes).

A satisfactory method trial has been conducted for permethrin per se on cottonseed (Pesticide Analytical Manual, Vol. II, Method I). A satisfactory method trial has been conducted for permethrin and its metabolites DCVA, 3-PBA, and 3-PBAcid in soybeans and liver (PP#8F2099, J. Onley, July 28, 1982).

6

RCB concludes that adequate analytical methods are available for enforcement of the proposed tolerances for permethrin and its metabolites DCVA and 3-PBA in cherries and plums.

Residue Data

Storage Stability

Storage stability studies were previously reviewed on lettuce, Brussels sprouts, and flue cured tobacco stored at 0 °F for approximately 19 months (PP#8F2034, A. Rathman, March 13, 1978) and on cottonseed (PP#7G1891, A. Rathman, March 10, 1977). No loss of permethrin occurred during storage in any of these commodities.

Storage stability of the primary metabolite DCVA and 3-PBA were determined on field treated green alfalfa, alfalfa hay, and lettuce stored at -20 °C (0 °F) for 33 months. The petitioner states that no residue decline was observed except for DCVA in lettuce (26%; 0.8%/month).

It appears that cherries and plums were stored for as long as approximately 17 months prior to analysis.

RCB concludes that available storage stability data are adequate.

Cherries

Five studies of Pounce 3.2 EC on cherries were conducted in the states of California, Washington, Oregon, New York, and Michigan. Three or four applications were made in the western United States (CA, WA, OR). Six applications were made in the eastern United States (NY and MI). All applications were foliar spray applications made with ground equipment. The application rate was 0.2 lb ai/A in all studies. Samples were taken at 0, 3, or 4, and 7 days after the last treatment in CA, WA, OR, and NY and at 0 and 3 days after the last treatment in MI. All cherry samples were frozen upon receipt at Princeton, New Jersey or Richmond, California and held at -18 °C until analysis. The majority of the residue was parent. Residues of the metabolites DCVA and 3-PBA were determined in two studies (WA and NY). Residues of metabolites in WA after four applications (including 0-, 3-, and 7-day PHI's) were ND-0.01 ppm DCVA and 0.02 ppm 3-PBA. Residues of metabolites in NY after six applications (including 0-, 4-, and 7-day PHI's) were ND-0.02 ppm DCVA and 0.06 to 0.10 ppm 3-PBA. Maximum residues (including parent, DCVA, and 3-PBA) resulting from 3 to 4 applications (WA) were 1.40 ppm (0-day PHI), 1.28 ppm (3-day PHI), and 1.29 ppm (7-day PHI). Maximum residues (including parent, DCVA and 3-PBA)

resulting from six applications (NY) were 4.12 ppm (0-day PHI), 2.29 ppm (4-day PHI), and 2.28 ppm (7-day PHI).

RCB concludes that residues resulting from the proposed use will not exceed the proposed tolerance of 3.0 ppm on cherries.

Plums and Prunes

Five studies of Pounce 3.2 EC on plums and fresh prunes were conducted in the states of CA, WA, NY, and MI. Three or four applications were made in the three studies conducted in the western United States (CA and WA). Seven applications were made in the two studies in the eastern United States (NY and MI). All applications were foliar spray applications made with ground equipment. The application rate was 0.2 lb ai/A in all studies. Samples were taken at 0, 3, or 4, and 7 or 8 days after the last treatment. All plum samples were frozen upon receipt at Princeton, NJ or Richmond, CA and held at -18 °C until analysis. The majority of the residue was parent. Residues of the metabolites DCVA and 3-PBA were determined in two studies (NY and CA). Residues of metabolites in NY after seven applications (including 0-, 3-, and 7-day PHI's) were ND (no detectable) DCVA and 0.03 to 0.04 ppm 3-PBA. Residues in CA after three applications (including 0-, 4-, and 7-day PHI's) were ND DCVA and 0.02 to 0.03 ppm 3-PBA. Maximum residues (including parent only) resulting from 3 to 4 applications (CA) were 0.38 ppm (0-day PHI), 0.20 ppm (3-day PHI), and 0.27 ppm (7-day PHI). Maximum residues (including parent, DCVA, and 3-PBA) resulting from seven applications (NY) were 0.59 ppm (0-day PHI), 0.82 ppm (3-day PHI), and 0.38 ppm (7-day PHI).

No residue data were submitted for dried prunes. A processing study on dried prunes is needed.

RCB concludes that residues resulting from the proposed use will not exceed the proposed tolerance of 1.0 ppm on plums. However, residue data for dried prunes processed from fresh fruit bearing residues at or near the proposed tolerance are needed. If there is a concentration of residues in dried prunes, then the petitioner will need to submit a proposal for an appropriate food additive tolerance.

Meat, Milk, Poultry, and Eggs

No food or feed items are involved in this proposed use on cherries and plums. No secondary residues are expected to occur in meat, milk, poultry, or eggs as a result of the proposed use. Therefore, this use falls in category 3 of Section 180.6(a) with respect to residues in meat, milk, poultry, and eggs.

Other Considerations

An International Residue Limit Status sheet is attached to this review. A Codex IRL has been proposed for permethrin on stone fruit at 2 mg/kg. A Canadian tolerance has been established for permethrin on plums at 0.5 ppm. No Mexican tolerances have been established for permethrin on plums or cherries.

Thus, the Codex proposal and Canadian tolerance are not compatible with the proposed United States tolerances on cherries and plums with respect to the tolerance expression and tolerance levels. Concerning the residue level for plums, RCB would have no objection to raising the level from the proposed 1.0 ppm level to 2 ppm, if toxicologically feasible, in order to coincide with the Codex proposal of a 2 mg/kg level on stone fruit.

cc: R.F., Circu., Reviewer-N.Dodd, EEB, EAB, PP#5F3271,
FDA, PMSD/ISB - Eldredge.
RDI:J.H.Onley:8/2/85:R.D.Schmitt:8/5/85
TS-769:RCB:CM#2:RM:810:x7484:N.Dodd:Kendrick & Co.:8/12/85

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL permethrin

CCPR NO. 120

PETITION NO 5F 3271

W. Gould
J. J. J.
7/20/80

Codex Status

☐ No Codex Proposal
Step 6 or above

Proposed U. S. Tolerances

Residue (if Step 9): _____

permethrin

Residue: permethrin and its metabolite

DCVA and (3-phenoxyphenyl) methanol

Crop(s) Limit (mg/kg)

stone fruit - 2

Crop(s) Tol. (ppm)

cherries 3.0

plums 1.0

CANADIAN LIMIT

Residue: _____

permethrin

MEXICAN TOLERANCIA

Residue: _____

Crop Limit (ppm)

plums 0.5

Crop Tolerancia (ppm)

none

Notes: