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

AUG 8 1988

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP8E3625. Permethrin on Cucurbits. Evaluation of Analytical Method and Residue Data. RCB No. 3644. MRID 405568-01, 405568-02, 405568-03, 405568-04, 405743-00, 405568-00

FROM: R. W. Cook, Chemist *RW Cook*
Petition Tolerance Section I
Residue Chemistry Branch
Hazard Evaluation Division

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

and

Toxicology Branch
Hazard Evaluation Division (TS-769C)

THRU: R. S. Quick, Section Head *RW*
Petition Tolerance Section I
Residue Chemistry Branch
Hazard Evaluation Division (TS-769C)

The petitioner, Professor G. M. Markle, National Coordinator and Dr. R. H. Kupelian, National Director, Interregional Research Project No. 4, State Agricultural Experiment Station, Rutgers University, New Brunswick, New Jersey 08903, on behalf of the IR-4 Project and the Agricultural Experiment Stations of Arkansas, California, Florida, Hawaii, Oklahoma, and Puerto Rico, and the United States Department of Agriculture proposes establishment of tolerances for residues of permethrin [(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] and the sum of its metabolites 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylic acid (DCVA) and (3-phenoxyphenyl)methanol (3-PBA) in or on the raw agricultural commodities (RACs) cucurbit vegetables at 3 ppm.

Residues of permethrin are currently regulated in Section 180.378(a), (b), and (c) of Title 40 of the Code of Federal Regulations (40 CFR 180.378) in a variety of raw agricultural crops including cantaloupes (3 ppm) and pumpkins (2 ppm).

Cucurbit vegetables group is specified in 40 CFR 180.34 (f) (9) (ix) (A):

Balsam pear (bitter melon) (Mormordica spp.); Chinese waxgourd (Chinese preserving melon) (Benicasa hispida); citron melon (Citrullus lanatus); cucumber (Cucumis spp.); gherkin (Cucumis anguria); gourds, edible (Lagenaria spp., Luffa acutangula, L. cylindrica); melons, including hybrids (Cucumis melo) (including cantaloupe, casaba, crenshaw, honeydew melons, honey balls, mango melon, muskmelon, Persian melon); pumpkin (Cucurbita spp.); squash, summer (Cucurbita pepo var. meloepo); squash, winter (Cucurbita maxima, C. moschata); watermelon, including hybrids (Citrullus spp.).

Representative crops in the cucurbit vegetables group are cucumbers, melons (cantaloupe or muskmelon), and summer squash.

The petitioner, IR-4, submits letters of authorization (1:FMC, Susan E. Burkart, Senior Registration Specialist, dated January 13, 1988; 2: ICI Americas, Inc., Diane L. Ierley, Pesticide Regulatory Specialist, dated January 14, 1988) addressed to Hoyt L. Jamerson.

Conclusions

1. The metabolism of permethrin in plants is adequately understood. The residues of concern are the parent compound, and its metabolites (DCVA) 3-(2,2-dichloroethyl)-2,2-dimethylcyclopropane carboxylic acid and (3-phenoxyphenyl) methanol (3-PBA).
2. Adequate methods are available for enforcement purposes in PAM II.
3. Residues of permethrin and its metabolites DCVA and 3-PBA are not likely to exceed the proposed cucurbit group tolerance of 3 ppm. Secondary residues of permethrin, if any, will not exceed the established tolerances in meat, milk, poultry, and eggs.
4. There are both Canadian and Codex tolerances for certain on the cucurbits at lower tolerance levels than those needed in the U.S. There are incompatibilities between the Codex, Canadian and U.S. tolerances which can not be resolved. A copy of the International Residue Limit Status sheet is attached.

Recommendations

We recommend for the proposed 3 ppm tolerance for the cucurbit vegetable crop group, TOX considerations permitting.

DETAILED CONSIDERATIONS

Manufacture and Formulation

The formulation proposed for use under this tolerance is Pounce\ 3.2 EC Insecticide, EPA Registration No. 279-3014, and contain 3.2 pounds of permethrin per gallon. We have previously concluded that no significant residue problems are anticipated from either the manufacturing impurities (if any) or the formulation inerts (if any).

Directions for Use (MRID 405568-00)

Pounce 3.2 EC

Cucurbit Vegetables: Balsam pear (Bitter Melon); Chinese Waxgourd (Chinese preserving melon); citron melon; cucumber; gherkin; gourds, edible; melons, including hybrids such as cantaloupe, casaba, crenshaw, honeydew melons, honey balls, mango melon, muskmelon, Persian melon; pumpkin; squash, summer and winter; watermelon, including hybrids: To control leafminers and squash bug - Use Pounce 3.2 EC at a rate of 8 ounces (0.2 pounds active) per acre). To control cabbage looper, cucumber beetle (adults), cutworms, melon worm, pickleworm, plant bugs (including Lygus and stink bugs), rindworms, and squash vine borer - Use Pounce 3.2 EC at a rate of 4 to 8 ounces (0.1 to 0.2 pound active) per acre. Apply a minimum of 4 gallons of finished spray per acre by air or 20 gallons of finished spray per acre with ground equipment. Do not apply more than 1.6 pounds active ingredient per acre per season. Pounce 3.2 EC may be applied up to harvest.

Cantaloupes: For general use directions, refer to the Cucurbit Vegetables crop grouping.

Pumpkins: For general use directions, refer to the Cucurbit Vegetables crop grouping.

We note the decrease from 1 day to 0 day for the preharvest interval.

Analytical Method (MRID 405568-04)

The analytical method used for the permethrin residue data is titled "Permethrin, Dichlorovinyl Acid and m-Phenoxy-benzyl Alcohol - Methodology for Cucurbits" by T.W. Armentrout and D.A. Kock [Analytical Bio-Chemistry Laboratories, Inc., P.O. Box 1097, Columbia, MO 65205] submitted to James C. Markle, FMC Corporation. The method bears the following designations "Study

Number 138CURR01"; "Final Report 35540-M"; "RC-0220"; and MRID "405568-04." No claim of confidentiality is made for any information contained in the report.

Procedures for Permethrin

Cucurbits are blended in hexane/propanol-2 and filtered. After reblending with additional solvent and filtration, the blending solutions were combined and partitioned with deionized water. The aqueous phase was then partitioned with hexane. After drying through anhydrous sodium sulfate, an aliquot of the sample was rotary-evaporated to about 2 to 3 mL of hexane. An activated florisil column was prewashed with 50 mL of hexane/methyl-t-butyl ether(9/1, v/v) followed by 10 mL hexane. The sample is eluted through the florisil column with the hexane/methyl t-butyl ether solution. The solution is reduced to 2 to 3 mL and brought to 6 mL for GLC analysis. Quantitation of permethrin per se (cis and trans isomers) was by gas chromatography using ^{63}Ni electron capture detector.

The method is reported to be sensitive to 0.05 ppm for each isomer, and residues are detectable at levels estimated at 0.01 ppm each isomer.

Procedures for Metabolites

A subsample (50 grams) is blended 5 minutes with 200 mL of methanol/water (2/1, v/v) and filtered. The filter cake is washed (50 mL) with the solvent mixture. The filtrate is made to 300 mL with extracting solution in 500 mL graduated cylinder. Separate aliquots for DCVA and 3-PBA residues are obtained.

For DCVA, the pH is adjusted to 8.3 with NaOH and partitioned twice with methylene chloride. The organic phase is reextracted with NaOH. The aqueous phases are combined and evaporated to 25 mL. Fortification of recovery samples occur at this point. Acid hydrolysis by HCl is followed by methylene chloride partition, reduction of sample volume and derivatization with pentafluorobenzyl bromide. The derivatized samples are then cleaned up on florisil column and eluted with 9/1 v/v hexane/ethyl ether prior to GC/mass spectra analysis.

For 3-PBA, the procedure is similar to DCVA but differs in that hexane is used to partition the basic solution, derivatization is by heptafluorobutyric anhydride and the florisil column is eluted with toluene.

Method sensitivity is reported to be 0.05 ppm for all compounds, with method detectability estimated at 0.01 ppm each permethrin isomer, 0.02 for 3-PBA and 0.03 ppm for each DCVA isomer. The report contains further details of the analytical procedure.

Recovery Data

Recovery data submitted in MRID 405568-04 for permethrin (cis + trans) 3-PBA, and cis-trans DCVA in melons, squash and cucumbers show:

	Recovery %		
	Melons	Squash	Cucumbers
cis-Permethrin	80 - 100	88 - 100	90 - 102
trans-Permethrin	80 - 98	86 - 98	85 - 96
PBA	92 - 129	75 - 108	70 - 120
cis-DCVA	86 - 100	80 - 106	70 - 101
trans-DCVA	92 - 114	78 - 110	75 - 110

Additional residue data for permethrin per se on cucumbers (MRID 405743-00) are derived by a different, published method: "Determination of FMC 33297 Residue in Plant, Animal, and Soil Matrices by Gas Chromatograph" (Fujie and Fullmer, J. Agric. Food Chem., Vol 26, No. 2, 1978, p. 395-398). We have previously concluded that this method is similar to those methods found in PAM-II (M. Firestone, 6/4/85, PP5E3225). For residues of 3-PBA and both cis and trans-DCVA, ICI method GRAM - 5/2 was used. This method "Gas Liquid Chromatographic Method for the Determination of Permethrin Metabolite in Crops," has been tested in our laboratory (actually, a version of this method) (see PP8F2099, 6/14/82, K. Zee).

Recovery studies submitted in MRID 405743-00 and MRID 405743-01 for cis-permethrin, trans-permethrin, cis DCVA, trans DCVA, and PBA in cucumbers and summer squash show overall:

	Method Recovery %	
	Cucumber	Squash
cis-permethrin	89 - 115	77 - 98
trans-permethrin	57 - 108	64 - 113
PBA	48 - 54	42 - 98
cis-DCVA	46 - 56	47 - 92
trans-DCVA	34 - 51	36 - 50

Storage Recovery %

cis-Permethrin	54 - 114	89 - 122
trans-Permethrin	62 - 122	70 - 96

We conclude that adequate methods are available for the enforcement of permethrin residues including metabolites, on cucurbits in PAM II.

Nature of the Residue in Plants

The metabolic fate of permethrin has been studied in a variety of plants: snap beans, cotton, soybeans, cabbage, and potatoes. These studies have shown permethrin is metabolized by ester hydrolysis to dichlorovinyl acid (DCVA, in cis- and trans-forms) and to m-phenoxybenzyl alcohol (PBA). Minor metabolites accounted for less than 5 percent each in several studies. Based on the studies, we have concluded that the residues of concern in plants are permethrin per se, DCVA, and 3-PBA.

Nature of the Residue in Animals

Cucurbits, melons, cucumbers, pumpkin, cantaloupe, and watermelon are not used for animal feed purposes, and therefore, the metabolism of permethrin in livestock animals is not germane to our concerns herein.

Magnitude of the Residue

Residue trials were conducted on cucumbers and summer squash in Florida during 1982 (MRID No. 405743-00 and 405743-01). Plot size was single row 10 ft long, containing 10 plants with 4 replicates. The concentration of the foliar dilute spray, applied by 2.5 gal hand held sprayer was 0.1, 0.2, or 0.4 lb per 100 gallons; the dilute spray was variously applied at rates of 60, 70, 85, or 100 gallons of spray per acre. Accordingly, less than the season maximum 1.6 pounds ai per acre was applied. Residue data for cis- and trans-permethrin, phenoxybenzyl alcohol, and cis- and trans-DCVA are derived by the methods discussed above regarding MRID Nos. 405743-00 and 405743-01 which see. Residues of PBA, cis- and trans-DCVA were undetectable at 1, 3, or 5 days after 1X or 2X application, except one sample showing 0.01 to 0.02 ppm of DCVA. Total residues of combined cis- and trans-permethrin were about 0.30 ppm or less from 1X application rate and 0.5 ppm from 2X application rate.

Similar studies were conducted on summer squash, with the same less-than-maximum application doses. Small amounts ≤ 0.08 ppm each of cis- and trans-permethrin PBA, cis-DCVA, or trans-DCVA were found in summer squash from both 1X and 2X application rates and all PHI intervals (1, 3, and 5 days).

Field residue trials were conducted on melons (MRID 405568-02) in 7 locations in 4 States (CA, NY, TX, IN) and residue samples taken at 0 and 3 days after final application of the total of 8 applications at 0.2 lb/A. Ground applications were used in 5 locations; 2 locations were aerial application. Melons treated included honeydew (1), cantaloupe (3), and watermelon (2), and unspecified (1). The unspecified melon is called "Superstar." We presume this is a cantaloupe even though the representative commodity is melons (cantaloupe or muskmelon). The melon samples were quartered and sections from at least four melons were frozen until analysis. We note that the 40 CFR

180.1(j) states that the RAC to be examined for pesticide residues shall be the whole RAC.

Residue levels (corrected for recovery) of cis- and trans-permethrin were ≤ 0.52 ppm and ≤ 0.63 ppm respectively, while residue levels of 3-PBA, cis-DCVA, and trans-DCVA were each < 0.05 ppm. Total residue levels of combined permethrin and metabolites ranged up to 1.2 ppm in an individual sample in unspecified ("Superstar") melons (presumably cantaloupes).

We note that watermelon showed the lowest residue levels (< 0.15 ppm) while honeydew and cantaloupe melons were intermediate in residue levels, and the unspecified ("Superstar", presumably cantaloupe) melons showed the highest residue levels.

Field residue trials were conducted on cucumbers (MRID 405568-01) in 6 locations in 4 States (CA, NY, TX, IN) and residue samples were taken at 0 and 3 days after final application of the total of 8 applications at 0.2 lb/A. Ground application equipment was used in 4 locations; aerial equipment was used in 2 locations.

Residue levels (corrected for recover) of cis- and trans-permethrin were about 0.52 ppm maximum. Residue levels of 3-PBA, cis-DCVA, and trans-DCVA were each < 0.06 ppm. Total permethrin residues ranged to 0.56 ppm.

Field residue trials were conducted on squash (MRID 405568-03) in 6 locations in 4 States (CA, TX, NY, IN) and residue samples were taken at 0 and 3 days after the last of 8 foliar applications at 0.2 lb ai/A/application. Squash fruit were quartered and quarter sections from 4 or more squash were combined prior to freezing. We note that whole RACs should be sampled for residue purposes. Residues of combined cis- and trans-permethrin were ≤ 0.44 ppm at 3 days. The residue of parent permethrin was equimixture of cis- and trans-isomers. Residues of 3-PBA ranged up to 0.15 ppm. For DCVA, the dominant isomer was trans-isomer at 0.12 ppm and < 0.05 ppm of cis-isomer. Total combined residue of permethrin (including cis- and trans-parent, cis- and trans-DCVA, and 3-PBA) was 1.2 ppm in squash harvested at 0 days after last application.

We note that one location, Phelps, NY, yielded the highest residue levels for squash, melons, and cucumbers.

Residues of permethrin in cantaloupes have been considered under PP5E3226 (see M.P. Firestone memoranda of October 16, 1985 and June 4, 1985). Maximum residues of permethrin (total) were found at 1.45 ppm (uncorrected for method recovery or storage recovery) in a Texas study with 7 applications of 0.2 lb ai/A and 3-day PHI. At 1 day PHI, maximum residue was 1.10. There are no data reported for the proposed 0-day PHI. When corrected for

method recovery and storage recovery, it was concluded that permethrin residues on cantaloupes could exceed 2 ppm, and a 3 ppm tolerance was recommended. We note that some samples considered in PP5E3226 were quartered in the field. Samples should be whole RAC, not quartered in the field.

Residues of permethrin in pumpkins have been considered under PP3E2861 which established tolerances to cover permethrin residues from a maximum of 4 applications of 0.2 lb ai/A, with a 1-day PHI. In brief, pumpkins in California contained 1.5 and 1.8 ppm from 4 applications while other locations showed 0.25 to 0.32 ppm total permethrin from the same application regimen. We are now asked to use these data in support of the proposed 8 application, 0-day PHI, 3 ppm group tolerance.

We conclude that combined residues of permethrin, 3-PBA, and DCVA will not exceed the proposed 3 ppm tolerance in the crop group cucurbit vegetables, when applied a maximum of 8 applications per season at 0.2 lb ai/A with a 0-day PHI.

Meat, Milk, Poultry, and Eggs

Some cucurbit vegetables such as melons or pumpkins are minor animal feed items. Tolerances for residues of permethrin in animal commodities are established to cover secondary residues from consumption of animal feed stuff bearing much higher residues of permethrin. For example, the animal feedstuffs corn forage and corn fodder both have tolerances at 60 ppm. We therefore conclude that residues of permethrin (combined) will not exceed established tolerances in meat, milk, poultry, or eggs.

OTHER CONSIDERATIONS

Removal of Residues

The petitioner reports that residues are not likely to exceed the proposed tolerance and therefore methods for removing the residue are unnecessary.

International Residue Limits

Codex residue limits for permethrin (as sum of isomers) are established at 0.5 mg/kg for cucumbers and gherkin, and 0.1 mg/kg for melons except watermelons. Canadian limits for residues of permethrin are 0.5 mg/kg for cucumbers. There are no Mexican limits for permethrin on subject crops. The above Codex and Canadian limits are not compatible with the U.S. crop group tolerance at 3 ppm for residues of permethrin, DCVA, and PBA. No pathway towards compatibility can be envisioned between the U.S. crop group tolerances and the Codex and Canadian single commodity

tolerances at this time. A copy of the International Residue Limit Status sheet is attached.

Attachment: Codex Sheet

cc: RWCook, PP8E3625, E. Eldredge (ISB/PMSD), Circ.(7), RF, TAS
(Arne), FDA

TS769:RCB:HED:RWCook:7/20/88:rwc:7/20/88:Rm810H:557-7324

RDI:Section Head:RSQuick:8/1/88:RDSchmitt:8/2/88

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Typing Corrected by R. W. Cook 7/20/88

Typing Corrected by R. W. Cook 8/8/88

Fred Stone
6/9/88

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Permethrin

CODEX NO. 120

CODEX STATUS:

No Codex Proposal
Step 6 or above

Residue (if Step 8):
permethrin (sum of isomers)

<u>Crop(s)</u>	<u>Limit (mg/kg)</u>
cucumber	0.5
gherkin	0.5
Melons, except watermelon	0.1

PROPOSED U.S. TOLERANCES:

Petition No. BE3625

RCB Reviewer RWCook

Residue: Permethrin DCVA + PBA per 180.378

<u>Crop(s)</u>	<u>Limit (mg/kg)</u>
Cucurbit crop group	3 ppm

CANADIAN LIMITS:

No Canadian limit

Residue: _____
permethrin

<u>Crop(s)</u>	<u>Limit (mg/kg)</u>
cucumbers	0.5

MEXICAN LIMITS:

No Mexican limit

Residue: _____

<u>Crop(s)</u>	<u>Limit (mg/kg)</u>
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NOTES: