



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

FEB 29 1988

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#8F3595/EPA Reg. No.s 279-3014, 279-3051.
Permethrin in or on Asparagus.
MRID No.s 404464-00 through 44464-04.
RCB No. 3306.
Evaluation of Analytical Methods and Residue Data.

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THROUGH: Charles L. Trichilo, Ph.D., Chief
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TO: George LaRocca, Product Manager No. 15
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and

Toxicology Branch
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FMC Corporation is requesting that a tolerance of 2.0 ppm be established for residues of permethrin [(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] and the sum of its metabolites, dichlorovinyl acid (DCVA) [3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid] and m-phenoxybenzyl alcohol (3-PBA) [(3-phenoxyphenyl)methanol], in or on the raw agricultural commodity (rac) asparagus. A tolerance of 1.0 ppm has already been established for this rac under 40 CFR 180.378. The PHI which corresponds to this tolerance is 3 days. Raising the tolerance would permit lowering of the PHI to 1 day.

A tolerance has been established for residues of permethrin on cottonseed at 0.5 ppm under 40 CFR 180.378(a). Tolerances have been established under §180.378(b) for the sum of residues of permethrin and its metabolites (DCVA and 3-PBA) for a number of racs. Tolerances range from 0.05 ppm in almonds, apples, corn grain, potatoes and soybeans to 60 ppm in corn fodder and corn forage. Finally, tolerances have been established for the sum of residues for permethrin, DCVA, 3-PBA and 3-phenoxybenzoic acid under §180.378(c) for animal commodities. Tolerances range from

0.05 ppm in eggs; poultry, fat; poultry, meat; and poultry, meat byproducts to 3.75 ppm in milk fat.

No Registration Standard has been issued on permethrin.

Conclusions

1. The nature of the residue expected in asparagus is adequately understood. The residue to be regulated is permethrin, DCVA and 3-PBA.
2. The nature of the residue in animals is adequately understood. The residue to be regulated is permethrin, DCVA, 3-PBA and 3-phenoxybenzoic acid. Since asparagus is not a normal animal feed item, large animal metabolism is not an issue in this petition.
3. Adequate analytical methods are available for enforcement purposes in the Pesticide Analytical Manual, Volume II (PAM II).
4. Permethrin is completely recovered by the Fat, Non-Fat and Luke multiresidue procedures in PAM I.
5. The description of the residue analyses is incomplete. The petitioner should report the dates of analysis of samples from each field trial. This conclusion does not affect Conclusion 7 on the adequacy of the proposed tolerance.
6. Existing storage stability data support the submitted residue data.
7. The proposed tolerance of 2.0 ppm for residues of permethrin and its metabolites in or on asparagus is appropriate.
8. Asparagus is not a normal animal feed item. Therefore, no residue in animal products from the proposed use is expected.
9. An International Residue Limit (IRL) Status sheet is appended to this review. There is a Codex tolerance of 1 ppm for permethrin alone (cis + trans isomers) and a Canadian negligible residue limit tolerance of 0.1 ppm for residues of permethrin on asparagus. Except for cottonseed, all crops listed in 40 CFR 180.378 have tolerances for permethrin and its metabolites. Since TOX has decided that the metabolites should be included in the tolerance expression, it would be inappropriate to specify a tolerance for parent only. We note, however, that even if in the future a tolerance is set

for permethrin only, the Canadian and the Codex tolerances would not be supported by the residue data submitted in this petition for permethrin alone.

Recommendation

With concurrence from TOX, RCB recommends that the proposed tolerance of 2.0 ppm for residues of permethrin and its metabolites in or on asparagus be established. However, we ask that the petitioner submit the data requested in Conclusion 5:

5. The petitioner should report the dates of analyses of samples from each field trial.

Detailed Considerations

Manufacture and Formulation

The manufacturing process for permethrin has been discussed previously by A. Rathman (PP#8F2034, memo dated 3/3/78).
Permethrin [REDACTED]

The purity of the technical product is 92%, and although there are over [REDACTED] in the technical material, these impurities should not form residue problems at the reported percentages.

The commercial products for which amended registrations are sought are Pounce 3.2 EC, which contains 38.4% permethrin (3.2 pounds active ingredient (ai) per gallon), and Pounce 25 WP, which contains 25.0% permethrin as active ingredient.

Proposed Use

To control cutworms and asparagus beetles ground apply Pounce 3.2 EC at a rate of 2-4 ounces per acre [0.05-0.1 lb ai/A] or Pounce 25 WP at a rate of 3.2-6.4 ounces per acre [0.05-0.1 lb ai/A]. Do not apply more than 0.4 lb ai/A per season. Do not apply within one day of harvest.

For post harvest application use Pounce 3.2 EC at a rate of 4 oz/A [0.1 lb ai/A] or Pounce 25 WP at a rate of 6.4 oz/A [0.1 lb ai/A]. Apply to the fern stage of the asparagus plant after spear harvest when larval and adult stage of the asparagus beetle, tarnished plant bug, lygus bug or Japanese beetle are present. (Permethrin may not be used to control the Japanese beetle in California.)

Nature of the Residue

Plants. The metabolic fate of permethrin has been studied on a variety of plants. Investigations involving cotton, beans,

potatoes, cabbage and soybeans have been previously reported (PP#7G1891, memo of A. Rathman, 3/10/77; PP#8G2029, memo of A. Rathman, 12/27/78; PP#8F2034, memo of A. Rathman, 3/13/78; PP#9F2196/FAP#9H5215, memo of J. Onley, 1/4/80; PP#0F2389, memo of J. Onley, 4/10/81). In all cases DCVA and 3-PBA were the two principal metabolites found, resulting from ester hydrolysis. Of the other metabolites isolated in the various studies, none were present in excess of 5% of the total residue. We conclude that the nature of the residue in plants is adequately understood. The residue to be regulated is permethrin, DCVA and 3-PBA.

Animals. Metabolism studies conducted in chickens, cows, goats and rats have been reviewed in PP#8F2034 (memo of A. Rathman, 3/13/78), PP#8F2044 (memo of A. Rathman, 4/24/78) and PP#9F2196 (memo of J. Onley, 1/4/80). For all species, these studies demonstrated that the terminal residues consisted of permethrin and the two plant metabolites DCVA and 3-PBA in all tissues. In addition, 3-PBA can be further degraded by oxidation to 3-phenoxybenzoic acid. This latter compound is included in the tolerances established in §180.378(c). The nature of the residue in animals is adequately understood. The residue to be regulated is permethrin, DCVA, 3-PBA and 3-phenoxybenzoic acid.

We note that because asparagus is not a normal animal feed item, large animal metabolism is not an issue in this petition.

Analytical Methodology

Permethrin (MRID No. 404464-03).

The analytical method appears as FMC Report RC-0023 and is entitled "Pounce^R Insecticide - Analytical Method for the Determination of Permethrin in/on Asparagus". The authors are T.W. Armentrout and D.A. Koch, and the date of the report is 9/21/87. No claim of confidentiality is made for any information contained in this study.

Twenty grams of macerated asparagus spears are blended for five minutes with 100 mL hexane/propanol-2 (2/1, v/v). The sample is filtered and the filter cake reblended for three minutes with an additional 100 mL solvent. The filtrates are combined and partitioned with 100 mL water. The water phase, in turn, is partitioned with hexane. The organic fractions are dried using sodium sulfate, then concentrated and cleaned up using a Florisil column. Samples are analyzed on a Tracor 560 Gas Chromatograph equipped with a ⁶³Ni electron capture detector and a column packed with 1% SP-2330 on Supelcoport (80/100 mesh).

The method is a modification of the procedure for cottonseed and soybeans given as Method I in PAM II. The extracting solvent was changed from methanol/water to hexane/propanol-2, and the gel permeation chromatography (GPC) purification step was omitted. A

method trial (of the method given in PAM II) for cis-permethrin and permethrin metabolites in soybeans and liver has been carried out (PP#8F2099/FAP#8H5190, memo of J. Onley, 7/28/82).

DCVA and 3-PBA (MRID No. 404464-04).

The analytical method for the two metabolites appears as FMC Report RAN-0200M and is entitled "Pounce^R Insectide - Analytical Method for the Determination of Dichlorovinyl Acid and m-Phenoxybenzyl Alcohol in/on Asparagus". The author is L.A. Rizzi, and the date of the report is 8/10/87. No claim of confidentiality is made for any information contained in this study.

The method for DCVA is similar but not identical to Method IIIA in PAM II. Samples are extracted with methanol/water followed by pH adjustment to 8.3, hexane partition (the hexane is discarded), acid hydrolysis, solid phase extraction using a C18 reverse phase column, and derivatization with pentafluorobenzyl bromide (PFB). The PFB derivatives are cleaned up on a Florisil column and then analyzed by GLC using a fused silica capillary with a 0.33u film of 5% phenyl 95% methyl silicone and Hewlett-Packard 5890 GC equipped with a HP 5970B Mass Selective Detector (MSD). The MSD is run in the Selected Ion Monitoring (SIM) mode. The method does not distinguish between DCVA and its conjugates.

The procedure for 3-PBA is virtually identical to that for DCVA except that the C18 cleanup step is omitted -- the acid hydrolysate is directly partitioned into methylene chloride -- and the selected ion monitored is different.

The detection limit for all three methods is reported to be 0.01 ppm.

Recoveries. Seven fortifications of permethrin were made at 0.05, 0.10, 0.20, 0.50 and 1.0 ppm. Recoveries averaged 91 $\pm$ 5% for cis-permethrin and 92 $\pm$ 6% for trans-permethrin.

Eight fortifications of DCVA were made at the 0.05 ppm or the 0.1 ppm level. Recoveries averaged 95 $\pm$ 14% for cis-DCVA and 92 $\pm$ 11% for trans-DCVA.

Six fortifications of 3-PBA were made at the 0.05 ppm, 0.06 ppm or 0.1 ppm level. Recoveries averaged 94 $\pm$ 13%.

Submitted chromatograms show clearly measurable peaks at the 0.05 ppm spiking levels.

Permethrin is completely recovered by the Fat, Non-Fat and Luke multiresidue procedures in PAM I.

Residue Data

Storage Stability. Storage stability data for field treated lettuce, brussels sprouts, tobacco and laboratory-fortified soybeans were submitted for PP#8F2034 (A. Rathman, memo of 3/13/78). At a storage temperature of -20°C, permethrin residue levels did not decline over a nineteen month period. Permethrin residues in cottonseed did not decline after six months at -20°C (PP#7G1891, A. Rathman, memo of 3/10/77).

In a third study field treated green alfalfa, alfalfa hay and lettuce were stored at -20°C and analyzed over 33 months for DCVA and 3-PBA. Both DCVA and 3-PBA showed no decline in either green alfalfa or alfalfa hay residues. DCVA levels in lettuce did decline at a slow rate (0.8% per month) (PP#5F3271, N. Dodd, memo of 8/14/85).

Two additional studies were reviewed in PP#6E3360 (N. Dodd, memo of 4/16/86). In the first study, field treated sorghum samples (grain, stover, forage) were stored at -10°F (except for temporary increases up to 40°F every 12 hours because of a frost-free feature of the refrigerator) for periods up to 52 months. No significant change in residue levels of permethrin occurred over this time, but variability was high (residue levels increased in some samples to a greater extent than they decreased in other samples).

In the second study, mustard greens, collard greens, turnip greens and turnip roots were fortified and stored at 0°F for 7-9 months. Recoveries were highly variable (37-118%), even within the same crop. Recoveries of metabolites (done for turnip roots and turnip greens) were more uniform (67-94%).

For the current petition field trials were conducted during 11985 and 1986. Samples were frozen immediately and shipped to the FMC laboratory in Richmond, CA in dry ice. Samples were stored at -18°C. Analyses were performed at ABC Laboratories in Columbia, MO. All analyses were completed by June 8, 1987. Thus the maximum time from sampling to analysis was about 27 months.

Storage stability data are adequate to support the asparagus residue data. However, the petitioner should report the date of analysis for each sample from the field trials so that we know the number of days from sampling to analysis for samples from each field trial. (This information is not necessary for our conclusion as to the adequacy of the proposed tolerance.)

For this petition eight field trials were carried out in six states: California, Washington, Minnesota, Georgia, Pennsylvania and Mississippi. According to the Foods and Food Production Encyclopedia, 1982, California and Washington account for about 75% of the asparagus production in the U.S. In only one of the

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eight trials was permethrin aerial applied. (The proposed Section B specifies ground application only.) In all cases the PHI was one day. Residue data in ppm are shown in Table 1. Except for the trial in Mississippi, where a total of 0.3 lb ai/A was applied, 0.1 lb ai/A was applied four times. Data have been corrected for percent recoveries.

Table 1

Location	Interval Between Apps. (days)	Permethrin		DCVA	3-PBA	Total ¹
		cis	trans			
El Centro, CA ²	7-9	0.62	0.62	ND	ND	1.24
Gonzales, CA	6-8	0.08	0.07	ND	ND	0.15
Prosser, WA	13-22	0.27	0.35	0.02	ND	0.62
Owatonna, MN	1-3	0.38	0.30	0.09	ND	0.76
Owatonna, MN	1-3	0.56	0.37	0.09	ND	1.00
Tifton, GA	1	0.59	0.41	0.05	0.02	1.07
Alburtis, PA	7	0.21	0.17	0.07	ND	0.44
Lexington, MS ³	3-11	0.22	0.17	0.02	ND	0.41

1. Maximum total for an individual sample, not a line total.
2. Aerial application.
3. Three applications of 0.1 lb ai/A.

These data support the proposed tolerance of 2.0 ppm.

Earlier residue studies were submitted in support of PP#3E2914, which resulted in the present tolerance of 1.0 ppm. The data were reviewed by J.E. Mayes in his memo of 11/28/83. Field trials were run in Hollister, CA; Lansing, MI; and Prosser, WA during the 1981 growing season. Permethrin was applied at the rate of 0.2 lb ai/A with from one to six applications. The PHI

was one day. Residue data in ppm are given in Table 2. No 3-PBA was detected.

Table 2				
<u>Location</u>	<u>No. of Apps</u>	<u>Permethrin</u>	<u>DCVA</u>	<u>Total</u>
California	1	0.11	0.04	0.15
	6	0.82	0.39	1.21
Michigan	4	0.43	0.10	0.53
Washington	1	0.61	0.22	0.83
	2	0.69	0.30	0.99
	6	0.32	0.06	0.38

A study was also conducted by Michigan State University in Oceanna County, MI in 1979. Four applications of 0.1 lb ai/A were made over a 7 day period. Samples were collected at 0 and 3 day PHIs. Surprisingly, residues from samples at the 3 day PHI were higher than those at 0 day PHI (0.44 ppm vs <0.02 ppm) (PP#3E2914, memo of 11/28/83).

The residue data submitted in PP#3E2914 are consistent with those submitted in this petition.

Meat, Milk, Poultry and Eggs

Because asparagus is not a normal animal feed item, no residue in animal products is expected from the proposed use of permethrin in/on asparagus.

Other Considerations

An International Residue Limit (IRL) Status Sheet is appended to this review. There is a Codex tolerance of 1 ppm for permethrin alone (cis + trans isomers) and a Canadian negligible residue limit tolerance of 0.1 ppm for residues of permethrin on asparagus. Except for cottonseed, all crops listed in 40 CFR 180.378 have tolerances for permethrin and its metabolites. Since TOX has decided that the metabolites should be included in the tolerance expression, it would be inappropriate to specify a tolerance for parent only. We note, however, that even if in the future a tolerance is set for permethrin alone, the Canadian and the Codex tolerances would not be supported by the residue data on permethrin per se submitted in this petition.

cc: Reviewer(Mike Flood), RF, Circu., TOX, PM#15, PP#8F3595,
ISB/PMSD(Eldridge).

TS-769C:RCB:Reviewer(MTF):CM#2:Rm810:557-4362:typist(mtf):2/29/88.

RDI:SectionHead:RSQuick:2/26/88:DeputyChief:RDSchmitt:2/26/88 .