PMSL/TS 8
1984

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

DEC 24 1987

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#8E3583/EPA Reg. No.'s 279-3014, 279-3051. Permethrin in or on Dry Bulb Onions and Garlic MRID No.'s 404040-00 thru 404040-02. RCB No. 3048 Evaluation of Analytical Methods and Residue Data.

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THROUGH: Robert S. Quick, Section Head
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TO: Hoyt Jamerson, PM-43
Emergency Response and Minor Use Section
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and

Toxicology Branch
Hazard Evaluation Division (TS-769C)

The Interregional Research Project No. 4 (IR-4) and the Agricultural Experiment Stations of New York and Oklahoma request the establishment of a tolerance of 0.1 ppm for the 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-dimethylcyclopropanecarboxylic acid (DCVA) and (3-phenoxyphenyl)methanol (3-PBA) in or on the raw agricultural commodities (rac's) onion (dry bulb) and garlic.

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 rac's. 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

(3-PBAcid) 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.

According to the Foods and Food Production Encyclopedia, 1982, dry onion production in 1976 was 1.7 million tons. In our opinion dry onions are not a minor food crop. "Dry onions" is not on the list of crops that EPA automatically considers for pesticide tolerances based on review of geographical limited data (51FR11341).

We note that under 40 CFR 180.1(h) tolerances established for dry bulb onions apply also to garlic.

Conclusions

1. RCB does not consider dry bulb onions to be a minor food crop.

2. The nature of the residue expected in onions and garlic is adequately understood. The residue of concern is permethrin, DCVA and 3-PBA.

3. The nature of the residue in animals is adequately understood. The residue of concern is permethrin, DCVA, 3-PBA and 3-PBAcid. Since onions and garlic are not normal animal feed items, large animal metabolism is not an issue in this petition.

4. Adequate analytical methods are available for enforcement purposes in the Pesticide Analytical Manual, Volume II (PAM II).

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

6. The description of the residue field trials is inadequate. The petitioner should submit additional details, such as plot dimensions, spacing of crops and volume pesticide applied per acre. The petitioner should also state whether the onions were planted as sets or seeds.

7. The proposed tolerance of 0.1 ppm for residues of permethrin and its metabolites in or on onions and garlic is appropriate. This conclusion is provisional pending a satisfactory response to Conclusion 6.

8. Dry bulb onions or garlic are not normal animal feed items. 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 Canadian negligible residue type limit of 0.1 mg/kg on permethrin, per se. Except for cottonseed, all rac's 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 should a tolerance of 0.1 ppm be set for parent only in the future, it would not need to be changed from the proposed tolerance of 0.1 ppm, which now includes metabolites.

Recommendation

RCB recommends against establishment of a tolerance for permethrin in or on onions for reasons stated in Conclusion 6:

6. The petitioner should submit additional experimental details of the residue field trials. Details should include plot dimensions, spacing of crops and volume pesticide applied per acre. The petitioner should also state whether the onions were planted as sets or seeds.

Detailed Considerations

Manufacture and Formulation

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

For control of onion thrips and armyworms spray Pounce 3.2 EC at a rate of 6-12 oz./A (0.15-0.3 lb ai/A) or Pounce 25 WP at a rate of 9.6-19.2 oz./A (0.15-0.3 lb ai/A). To control cutworms, leafminers, onion maggots (adults) and stink bugs use Pounce 3.2 EC at a rate of 4-12 oz./A (0.1-0.3 lb ai/A) or Pounce 25 WP at a rate of 6.4-19.2 oz./A (0.1-0.3 lb ai/A).

Apply in a minimum of 20 gallons of water per acre as a foliar spray with ground equipment.

Do not apply more than 2.4 lb ai/A/season.

Do not apply within 1 day of harvest.

Do not graze livestock in treated areas or cut treated crops for food.

Nature of the Residue

Plants. The metabolic fate of permethrin has been studied on a variety of plants. Investigations involving cotton, beans, potatoes, and cabbage have been previously reported (PP#7G1891, memo of A. Rathman, 3/10/77; PP#8G2029, memo of A. Rathman, 12/27/78; 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 in adequately understood. The residue of concern in 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) and in PP#8F2044 (memo of A. Rathman, 4/24/78). 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 of concern is permethrin, DCVA, 3-PBA and 3-PBAcid.

We note that because neither onions (dry bulb) nor garlic are normal animal feed items, large animal metabolism is not an issue in this petition.

Analytical Methodology

The analytical method used to generate the permethrin residue data in the petition is given in Volume 3 of the petition (MRID No. 404040-02). The report is entitled "Methodology for the Determination of Permethrin, Dichlorovinyl Acid and m-Phenoxybenzyl Alcohol Residues in/on Onion Bulbs", FMC Report RAN 0199M, 6/18/87. The author is J.W. Stearns. No claim of confidentiality is made for any information contained in this study.

Permethrin. Macerated onion samples were blended for five minutes with 100 mL hexane/propanol-2. The sample was filtered and blended again with solvent. The solvent fractions were combined and partitioned with water. The water phase, in turn, was partitioned with hexane. The organic fractions were dried

using sodium sulfate, then concentrated and cleaned up using gel permeation and Florisil columns. Samples were analyzed using a Hewlett Packard 5730 GC equipped with a ^{63}Ni electron capture detector and a column packed with 1% SP 2330 coated on Supelcoport 80/100 mesh.

The method is a modification of the procedure for cottonseed and soybeans given in PAM II. The extracting solvent was changed from hexane to hexane/propanol-2. A method trial 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. The procedure for the analysis of DCVA is similar to that described in PAM II. Samples were extracted with methanol/water, followed by pH adjustment to 8.3, hexane wash (the hexane is discarded), acid hydrolysis, organic partition using methylene chloride and derivatization with pentafluorobenzyl bromide (PFB). The PFB derivatives were cleaned up with a Florisil column and then analyzed by GLC using a fused silica capillary with 0.33 u film of 5% phenyl 95% methyl silicone and a Hewlett-Packard 5890 GC equipped with a Hewlett-Packard 5970B Mass Selective Detector, run in the selected ion monitoring (SIM) mode.

The method does not distinguish between DCVA and its conjugates.

3-PBA. The procedure is virtually identical to that for DCVA except for the selected ion monitored.

Recoveries. Nine fortifications of permethrin in onions were made at 0.05 ppm or 0.1 ppm. Recoveries averaged 79±7% for cis-permethrin and 79±9% for trans-permethrin. (Analytically pure cis and trans separate standards were used in the fortifications.)

Twelve fortifications for DCVA in onions were made at 0.05 ppm. Recoveries averaged 103±9% for cis-DCVA and 107±8% for trans-DCVA.

Nine fortifications for 3-PBA in onions were made at 0.05 ppm. Recoveries averaged 103±12%.

Submitted chromatograms show clearly measurable peaks at both 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 occurred over this time, but variability was high (residue levels increased in some samples to a greater extent than they decreased in other samples), and the initial residue levels were not reported.

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%).

In the residue study for this petition, onions were analyzed at times up to 12 months after sampling. Onion tops and roots were removed in the field, and the bulbs frozen immediately. Samples were shipped to FMC laboratories in Richmond, CA by packing in dry ice. Upon receipt, samples were stored at -18°C until analysis. Available storage stability data support the stability of the residues under these conditions.

Residue data appear in FMC Report RAN 0199 authored by J.W. Stearns entitled "Determination of Permethrin, Dichlorovinyl Acid and m-Phenoxybenzyl Alcohol Residues in/on Onion Bulbs", 10/16/87. The report has been assigned MRID No. 404040-01.

Sixteen residue trials were conducted during 1986 in the following nine states: California, Colorado, Idaho, Michigan, New Jersey, New York, Texas, Wisconsin and Washington. According

to Agricultural Statistics, 1985. These nine states are all among the top 15 onion growing states. Six of the trials were conducted using Pounce 25 WP, and were at locations where trials using Pounce 3.2 EC were also conducted. Eight applications of 0.3 lb ai/A were made at time intervals varying from 3 to 18 days (7-10 days was typical). All trials were conducted using ground application equipment.

The petitioner should submit more detailed descriptions of the field trials, such as plot dimensions, spacing of crops and volume pesticide per acre.

Planting occured two to five months before sampling, with 4 months being typical. For this reason, it is likely that in all but two field trials (#'s 3 and 9) the onions were planted from seeds. According the our Cultural Practices File, onions grown from seed are generally harvested 95-120 days after planting; onions grown from sets are generally harvested 60-75 days after planting. Nevertheless, the petitioner should state whether onions were planted as seeds or as onion sets.

Data are summarized in Table 1. Results have been corrected for average method recoveries.

Table 1

Trial No.	Site	EC/WP	PHI	Permethrin cis	Permethrin trans	DCVA cis	DCVA trans	3-PBA
1	Princeton, NJ	EC	0	ND	ND	ND	ND	ND
2		WP	0	ND	(0.01)	ND	ND	ND
3	Walla Walla, WA	EC	0	ND	(0.02)	ND	ND	ND
4	Escalon, CA	EC	0	(0.04)	0.05	ND	ND	ND
			7	ND	(0.02)	(0.01)	(0.01)	ND
			14	ND	ND	ND	ND	ND
5	Parma, ID	EC	0	ND	ND	ND	ND	ND
6	Longmont, CO	EC	0	ND	ND	ND	ND	ND
7	Uvalde, TX	EC	0	(0.04)	(0.04)	ND	(0.01)	ND
			7	(0.02)	(0.02)	ND	ND	ND
			14	ND	ND	ND	(0.01)	ND
8		WP	0	(0.01)	(0.01)	ND	(0.01)	ND
			7	ND	ND	ND	ND	ND
			14	ND	ND	ND	ND	ND
9	Middleton, WI	EC	0	(0.02)	(0.04)	ND	ND	ND
			7	ND	(0.02)	ND	ND	ND
			15	ND	(0.02)	ND	ND	ND
10		WP	0	(0.03)	(0.04)	ND	ND	ND
			7	ND	ND	ND	ND	ND
			15	ND	ND	ND	ND	ND
11	Oregon, WI	EC	0	(0.02)	(0.03)	ND	ND	ND
12		WP	0	0.05	(0.04)	ND	ND	ND
13	Marcellus, MI	EC	0	ND	(0.01)	ND	ND	ND
14		WP*	0	ND	ND	(0.01)	ND	ND
15	Pine Island, NY	EC	0	ND	ND	ND	ND	ND
			7	ND	ND	(0.01)	ND	ND
			14	ND	ND	(0.01)	ND	ND
16		WP	0	ND	(0.01)	ND	ND	ND
			7	ND	ND	ND	ND	ND
			14	ND	ND	ND	ND	ND

* The petition table has both field trials in Michigan conducted using the EC formulation. This was corrected in a 12/15/87 telephone conversation with Dr. George M. Markle of IR-4 (201-932-9575).

All but two analyses failed to show levels of permethrin or its metabolites at or above the quantitation limit of 0.05 ppm.

No residue data have been submitted for garlic. Garlic is similar to dry bulb oinions (growing period, both root crops), and since permethrin is primarily a surface residue and garlic

sheaths are removed before crop analysis, we are translating the dry bulb oinion residue data to garlic.

Based on these data RCB concludes that the proposed tolerance of 0.1 ppm is appropriate. This conclusion is provisional pending submission of additional details of the field trials.

Meat, Milk, Poultry and Eggs

Because neither dry bulb onions nor garlic are normal animal feed items, no residue in animal products is expected from the proposed use of permethrin.

Other Considerations

An International Residue Limit (IRL) Status sheet is appended to this review. There is a Canadian negligible residue type limit of 0.1 mg/kg for permethrin per se on onions. Except for cottonseed, all rac's 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, it would be inappropriate to specify a tolerance for parent only. We note, however, that should a tolerance of 0.1 ppm be set for parent only at some time in the future, it would not need to be changed form the proposed tolerance of 0.1 ppm, which now includes metabolites.

cc: Reviewer(Mike Flood), RF, Circu., TOX, PM#43, PP#8E3583, ISB/PMSD(Eldridge).

TS-769C:RCB:Reviewer(MTF):CM#2:Rm810:557-4362:typist(mtf):12/23/87.
RDI:SectionHead:RSQuick:12/23/87:DeputyChief:RDSchmitt:12/23/87.