11-6-92

Residue Chemistry Review

Comments:

Subject: PP#2F4100. Lambda-cyhalothrin in/on Dry Onion Bulbs and Garlic. Evaluation of residue data and analytical methodology. CBTS# 9440. HED# 2-1506. MRID#'s 422068-01, -02, -03.

Document Class:

Product Chem:

Residue Chem: 860.1200 Directions for use
860.1500 Crop field trials
860.1550 Proposed tolerances

Biochemicals:

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Commodities: Onion, dry bulb; Garlic

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Reviewers: José J. Morales

Review Approver: Debra Edwards **Approved on:** November 6, 1992

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MEMORANDUM:

SUBJECT: **PP#2F4100**. Lambda-cyhalothrin in/on Dry Onion Bulbs and Garlic. Evaluation of residue data and analytical methodology. CBTS# 9440. HED# 2-1506. DP Barcode D174919. MRID#'s 422068-01, -02, -03.

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ICI Agricultural Products is requesting the establishment of tolerances for lambda-cyhalothrin ([1alpha-(S), 3alpha-(Z)]-(±)-cyano-(3-phenoxyphenyl)methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate) in/on dried onion bulb and garlic at 0.10 ppm. Tolerances with an expiration date of August 30, 1991 were established under 40 CFR §180.438 for the fat, meat and mbyp of cattle, goats, hogs, horses and sheep at 0.01 ppm; milk at 0.01 ppm; and cottonseed at 0.05 ppm. Raw Agricultural Commodities (racs) for which tolerances are pending include soybeans (PP#7F3488); wheat, sweet corn and sunflowers (PP#7F3560/7H5543); broccoli, cabbage and tomatoes (PP#1F3952/1H5607); and head lettuce (PP#1F3985).

A food additive tolerance of 10.0 ppm in/on dried hops was recently established under 40 CFR §185.1310 as a result of FAP#0H5599 (57 FR 32440).

CONCLUSIONS

1. The manufacturing process of technical grade lambda-cyhalothrin has been adequately described. We do not foresee any residue problems from impurities in the technical. Although deficiencies pertaining to the written confirmation from the Chemical Abstract Service are resolved; CBTS recommends that the IUPAC names for lambda-cyhalothrin and its epimer (rather than the Chemical Abstract names) appear in the regulation, since in our opinion, a practicing chemist can more readily relate the IUPAC name to the structure (refer to M. Flood's memo of 3/23/92 for more details and the IUPAC names for lambda-cyhalothrin and its epimer).

2a. The nature of the residue in plants is adequately understood. The residue to be regulated is lambda-cyhalothrin, per se, and its epimer.

2b. Since dry onion bulbs and garlic are not animal feed items, no secondary residues in animals are anticipated from the proposed use.

3a. ICI Method 81 for parent lambda-cyhalothrin and its epimer in plant matrices has undergone successful EPA method validation.

3b. Recoveries have been determined under FDA's multiresidue protocols for cyhalothrin, CPA [Cis-1-RS-3-(ZE-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid] and 3-PBAcid [3-phenoxybenzoic acid] (these recoveries were not listed in FDA's 11/2/90 summary).

4. Geographical representation of residue data is adequate for the proposed use on dry onion bulbs and garlic.

5. The storage stability data of lambda-cyhalothrin on dry onion bulbs are adequate to support the residue analyses for parent and epimer but not the metabolites. The petitioner needs to submit storage stability data of metabolites CPA, 3-PBAcid and 3-PBAlcohol [3-phenoxybenzyl alcohol] for periods up to 26 months and in extracts for up to 42 days (the conclusion that the residue to be regulated consists only of parent and epimer was made under the assumption that the residue data on metabolites were accurate).

6. The residue data indicate that lambda-cyhalothrin residues will not exceed the proposed tolerance of 0.10 ppm for garlic and dry onion bulbs.

7. An International Residue Limit (IRL) Status Sheet is appended to this review. There are no Codex, Canadian or Mexican Limits established for lambda-cyhalothrin on garlic and dry onion bulbs. Therefore, no compatibility problems exist.

RECOMMENDATION

CBTS recommends against the proposed tolerance for reasons given in Conclusion 5.

DETAILED CONSIDERATIONS

PRODUCT CHEMISTRY

The manufacturing process for lambda-cyhalothrin was submitted in support of PP#6F3318 (MRID# 401820-01) and discussed in S. Willett's memo of 9/29/87. There are no toxicological concerns for any of lambda-cyhalothrin impurities. Discussion about structure and isomers appears in M. Flood's memo of 9/19/91 (PP#7F3560/7H5543).

CBTS concludes that the manufacturing process of technical grade lambda-cyhalothrin has been adequately described. We do not foresee any residue problems from impurities in the technical. Although deficiencies pertaining to the written confirmation from the Chemical Abstract Service are resolved; CBTS recommends that the IUPAC names for lambda-cyhalothrin and its epimer (rather than the Chemical Abstract names) appear in the regulation, since in our opinion, a practicing chemist can more readily relate the IUPAC name to the structure (refer to M. Flood's memo of 3/23/92 for more details and the IUPAC names for lambda-cyhalothrin and its epimer).

PROPOSED USE

The registered formulation of lambda-cyhalothrin proposed for use is Karate®. Karate® (EPA Reg. No. 10182-96) is an emulsifiable concentrate containing 13.1% of ai and 86.9% of inerts. This formulation contains 1 pound of active ingredient per gallon.

The following directions apply for onions (dry bulbs) and garlic: to control cutworms, seedcorn maggot adults, onion maggot adults and leafminer adults apply 0.015 to 0.025 lbs. ai/A. For control of armyworms, onion thrips, western flower thrips, aphids, plant bugs and stink bugs apply 0.02 to 0.03 lbs. ai/A. Apply as required by scouting, usually at intervals of 5 or more days. Apply with ground or air equipment using sufficient water and application methods to obtain full coverage of foliage. When applying by air, apply in a minimum of 2

gallons water per acre. Do not apply within 14 days of harvest. Do not apply more than 0.24 lbs. ai/A/season.

NATURE OF THE RESIDUE

Plants

Data on plant metabolism show that lambda-cyhalothrin is metabolized by cleavage of the ester linkage to form cyclopropane carboxylic acids and the corresponding phenoxybenzoic acid and/or 3-phenoxybenzyl alcohol (M. Flood's memo of 1/22/92).

CBTS concludes that the nature of the residue in plants is adequately understood. The residue to be regulated is lambda-cyhalothrin, per se, and its epimer.

Animals

Since dry onion bulbs and garlic are not animal feed items, no secondary residues in animals are anticipated from the proposed use.

ANALYTICAL METHODOLOGY

The analytical methodology used to determine the residues of lambda-cyhalothrin and its epimer in plant matrices is ICI Method 81, which was first described in MRID# 400540-01. Briefly, samples were extracted with acetone:hexane 1:1 (v/v), coextracted lipids were removed by liquid-liquid chromatography, followed by a florisil column to remove endogenous materials. The final determination is made by capillary GC with electron capture detection. The limit of determination is 0.01 ppm. This method has undergone EPA Method Validation for soybeans (PP#6F3318/PP#7F3488, E. Greer memo of 9/30/87).

The analytical methodology used for determination of lambda-cyhalothrin metabolites was submitted in FAP#0H5599 (MRID#416146-03). This method provides the co-analysis of cis and trans CPA (PP890). Lambda-cyhalothrin includes the cis isomer only. The trans configuration is in lower amounts, and it is believed to result from photoisomerization of the metabolite on the plant surface. The analysis of 3-phenoxybenzoic acid (3-PBAcid) and 3-phenoxybenzyl alcohol (3-PBAlcohol) can be carried out by this methodology. 3-PBAlcohol is oxidized to 3-PBAcid and the 3-PBAcid residue is quantified. Data are reported as the combination of 3-PBAcid and 3-PBAlcohol. Briefly, samples are extracted, filtered and subjected to a C_{18} solid phase extraction. The extract is rotoevaporated, concentrated with HCL

and refluxed for 2 hours. After cooling, the extract is partitioned with organic solvent and the aqueous phase is discarded. Jones reagent (23 mL of concentrated sulfuric acid, 77 mL of water and 24g of chromium (VI) oxide) is added to the organic phase and after the reaction is carried out, the extract is diluted with water and partitioned with organic solvent. The organic layer extract is acid washed and then partitioned with tetraborate buffer (pH 9.0). The aqueous layer is retained, acidified, and partitioned with dichloromethane. The extract is evaporated to dryness and derivatized with trifluoroacetic anhydride and trifluoroethanol at 100°C for 5 minutes. This derivatized extract is analyzed by capillary GC using a mass selective detector. The limit of determination is 0.01 ppm.

MULTIRESIDUE TESTING

The petitioner has determined recoveries of cyhalothrin, PP890 and 3-PBAcid under FDA's multiresidue protocols (PP#7F3488, S. Willet's memo of 3/15/88; PP#7F3560/7H5543, M. Flood's memo of 9/19/91). As of 11/2/90, results have not been listed in FDA's summary.

RESIDUE DATA

Residue data reflecting the application of lambda-cyhalothrin to dry onion bulbs appear in the following report:

> "Lambda-cyhalothrin (ICIA0321): Magnitude of the Residue Study on Dry bulb onions"; J.C. Mckay; 2/11/92; Laboratory Project ID Nos. 0321-90-MR-06 and 0321-90-MR-09. Report No. RR 91-062B. Performing Laboratory was ICI Americas Inc. Western Research Center, Environmental Chemistry Analytical Section, Richmond, CA (MRID# 422068-03).

Ten field trials were conducted during 1990 in California, Colorado, Idaho, Michigan, New York, Oregon, and Texas. According to Agricultural Statistics, 1988, these states accounted for at least 87% of the dry onion bulb production in the U.S. Eight applications of lambda-cyhalothrin, using ground equipment, were made at a rate of 0.03 lbs. ai/A (1X) with a five to eight day interval between them. In two of the trials, aerial application of lambda-cyhalothrin was made using a total of 2.0 gallons per acre. In the Idaho trial, the interval between the first and second application was 15 days, the other subsequent applications were made at 7 day intervals. In the Oregon trial, lambda-cyhalothrin was applied at a rate of 0.06 lbs. ai/A (2X). Dry onion bulbs were harvested within 14 days after the last application of lambda-cyhalothrin in all field trials. After collection, samples were frozen and shipped to ICI Americas Inc. Western Research Center, Environmental Chemistry Analytical Section, Richmond, CA.

No residue data were sent for garlic. The petitioner claims that 40 CFR §180.1(h) specifies that a tolerance for dry bulb onions applies to garlic and that they are relying on the magnitude of the residue data developed for dry onion bulbs to support the use of lambda-cyhalothrin on garlic.

CBTS concludes that geographical representation of residue data is adequate for the proposed use on dry onion bulbs and garlic.

Residues of lambda-cyhalothrin were shown to be stable when stored at -18°C for up to 26 months in commodities like peach, pea, oil seed rape, wheat grain, sugarbeet root, cottonseed, apple, cabbage and potatoes (PP#0H5599, M. Flood's memo of 9/19/91). To assess stability in extracts, 1:1 acetone:hexane extracts from the treated racs were held at <4°C for 33 to 42 days after the 26 months analyses. No significant degradation was seen in these extracts. Samples of dry onion bulbs were analyzed for lambda-cyhalothrin residues up to almost 13 months after sampling. Maximum interval between extraction and analyses was 14 days. Storage stability of metabolites PP890, 3-PBAcid and 3-PBAlcohol in 13 racs has been reported in PP#1F3952/1H5607. Metabolite residues were stable at -20 $\pm$ 10°C for 3 months. Data to support the stability of the metabolites for longer periods are being developed. Samples of dry onion bulbs were analyzed for lambda-cyhalothrin metabolites PP890, 3-PBAcid and 3-PBAlcohol up to almost 14 months after sampling. Maximum interval between extraction and analyses was 11 days.

CBTS concludes that the storage stability data of lambda-cyhalothrin on dry onion bulbs are adequate to support the residue analyses for parent and epimer but not the metabolites. The petitioner needs to submit storage stability data of metabolites CPA, 3-PBAcid and 3-PBAlcohol for periods up to 26 months and in extracts for up to 42 days (the conclusion that the residue to be regulated consists only of parent and epimer was made under the assumption that the residue data on metabolites were accurate).

Recovery data were obtained from untreated samples fortified with lambda-cyhalothrin at the level of 0.04 ppm to 0.09 ppm. Overall recoveries of 75% to 105% were obtained. Recovery data for lambda-cyhalothrin epimer at fortification levels of 0.06 ppm to 0.11 ppm were of 86% to 103%. Recovery data for metabolites PP890, 3-PBAcid, and 3-PBAlcohol at fortification levels of 0.01 ppm to 0.05 ppm ranged from 73% to 116% for PP890, 85% to 91% for 3-PBAcid, and 82% to 92% for 3-PBAlcohol. Submitted chromatograms show well resolved peaks in support of this data.

Table I summarize the amount of residues on dry onion bulbs resulting from 8 applications of lambda-cyhalothrin at the rate of 0.03 lbs. ai/A.

Table I. Lambda-cyhalothrin residues on dry onion bulbs

Study Location	Application Method[1]	PHI	ICIA0321 (ppm)[2]	R157836 (ppm)[3]	PP890 (ppm)[4]	3-PBAcid (ppm)[5]
CA	control	--	<0.01	<0.01	<0.01	<0.01
	G	14	0.05,0.06	0.01	<0.01	<0.01
CA	control	--	<0.01	<0.01	--	--
	G	14	<0.01	<0.01	--	--
CO	control	--	<0.01	<0.01	--	--
	G	14	<0.01	<0.01	--	--
MI	control	--	<0.01	<0.01	<0.01	<0.01
	G	14	0.05,0.06	0.01	0.02	<0.01
NY	control	--	<0.01	<0.01	<0.01	<0.01
	G	14	0.04	<0.01	<0.01	<0.01
OR[6]	control	--	<0.01	<0.01	<0.01	<0.01
	G	14	0.02	<0.01	0.01	<0.01
ID	control	--	<0.01	<0.01	<0.01	<0.01
	G	14	0.01	<0.01	<0.01	<0.01
TX	control	--	<0.01	<0.01	--	--
	G	14	<0.01	<0.01	--	--
CA	control	--	<0.01	<0.01	<0.01	<0.01
	A	14	0.05	<0.01	<0.01	<0.01
CO	control	--	<0.01	<0.01	--	--
	A	14	<0.01	<0.01	--	--

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1. G - ground A - aerial
2. Lambda-cyhalothrin
3. epimer of lambda-cyhalothrin
4. cis-isomer
5. 3-Phenoxybenzoic Acid (combination of 3-PBAlcohol + 3-PBAcid)
6. Lambda-cyhalothrin was applied at 0.06 lbs. ai/A (2X rate)

Maximum lambda-cyhalothrin and metabolite residues resulting from 8 applications of Karate® at 0.03 lbs. ai/A were 0.06 ppm for lambda-cyhalothrin per se, 0.01 ppm for lambda-cyhalothrin epimer, 0.02 ppm for the cis-isomer PP890, and <0.01 ppm for 3-PBAcid.

The residue data indicate that lambda-cyhalothrin residues will not exceed the proposed tolerance of 0.10 ppm for garlic and dry onion bulbs. Pending submission of adequate storage stability data for lambda-cyhalothrin metabolites, CBTS could recommend in favor of the proposed tolerance for lambda-cyhalothrin on garlic and dry onion bulbs at 0.10 ppm.

OTHER CONSIDERATIONS

An International Residue Limit (IRL) Status Sheet is appended to this review. There are no Codex, Canadian or Mexican Limits established for lambda-cyhalothrin on garlic and dry onion bulbs. Therefore, no compatibility problems exist.

Attachment: International Residue Limit Status Sheet

cc: SF, RF, Circu., José J. Morales, M. Flood, E. Haeberer, PP#2F4100

H7509C: Reviewer (JJM): CM#2: Rm 804-Q: 305-5010: typist (JJM): 10/1/92

RDI: E. Haeberer (10/8/92): M. Flood (10/2/92): R. Loranger (10/13/92)