



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

AUG 18 1995

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM:

SUBJECT: **Permethrin.** Storage Stability of Permethrin Metabolites in Racs. GLN: 171-4(e). Chemical No. 109701. Case No. 2510. MRID No. 42919201. CBRS No. 16025. DP Barcode: D218416.

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BACKGROUND

Zeneca Ag (formerly ICI) has submitted storage stability data for metabolites of permethrin on various racs in response to the Phase IV review on permethrin (C. Olinger & S. Funk 5/10/91). Thirteen crops were analyzed for DCVA, 3-PBA and 3-phenoxybenzoic acid and PP890. PP890 is not a regulated metabolite, and therefore; not considered in this review.

The nature of the residue in plants is adequately understood. The qualitative nature of the residue in animals is not adequately understood. A poultry metabolism study using dermal treatment and ruminant metabolism studies using both oral dosing and dermal treatment are under review in CBRS.

One GLC/MS method and six GLC/electron capture detector (ECD) methods are listed in



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PAM, Vol. II (Sec. 180.378) for the determination of permethrin and its regulated metabolites in/on plant (Methods I, II, III, and IIIa) and animal (Methods II, IV and A) commodities. These GLC methods have undergone EPA validation and have been deemed adequate for enforcement purposes.

Tolerances for residues of permethrin [(3-phenoxyphenyl)methyl-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylate] in/on cottonseed are expressed in terms of permethrin *per se* [40 CFR§180.378 (a)]. Tolerances for permethrin residues in/on other plant RACs are currently expressed as the sum of permethrin and its metabolites, 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylic acid (DCVA) and (3-phenoxy-phenyl) methanol (3-PBA) [40 CFR §180.378 (b) and (d)]. Tolerances for permethrin residues in/on animal commodities are expressed as the sum of permethrin and its metabolites, DCVA, 3-PBA and 3-phenoxybenzoic acid [40 CFR§180.378 (c)].

CONCLUSIONS

1. Residues of the following metabolites of permethrin were stable in all racs tested for a period of 36 months stored at -20°C: DCVA, 3-PBA and 3-phenoxybenzoic acid. These storage stability study results support the residue trial data submitted for permethrin reregistration.

RECOMMENDATIONS

The registrant(s) should be advised that the data on the storage stability of permethrin metabolites: DCVA (cis + trans), 3-PBA and 3-phenoxybenzoic acid in various racs are adequate and no further data regarding storage stability on these metabolites are required. Additional metabolite storage stability data for processed commodities and animal commodities may be required.

DETAILED CONSIDERATIONS

Untreated field samples of thirteen (13) racs were collected and separately homogenized prior to fortification individually with DCVA, 3-PBA (alcohol) and 3-phenoxybenzoic acid. The 13 racs were: apples, cabbage, corn fodder, corn forage, cottonseed, lettuce, peanut hulls, peanut meats, sorghum grain, soybeans, sugar beets, tobacco and tomatoes. Approximately 10 g of each rac was chopped and then fortified with 1 ml of a solution containing 1 ug/ml of DCVA, a separate 10 g of each rac was then chopped and fortified with 1 ml of a solution containing 1 ug/ml of 3-PBA, and the same procedure was used to fortify rac samples with 3-phenoxybenzoic acid. The final fortification level in each spiked rac sample was 0.10 ug/g (ppm).

The "zero-day" fortified samples were extracted on the day of fortification and stored at -20°C ± 5°C until analyzed a few days later. The remaining samples were stored as above and extracted and analyzed at 3-5, 12-14, 24-26 and 36 month intervals. Analysis followed within

a few days of extraction. Duplicate samples were analyzed. The analytical method's limit of quantitation was 0.01 ppm. Adequate sample chromatograms and calculations were provided.

Analytical Method

The homogenized sample is extracted with acetonitrile, homogenized again with acetonitrile/water (pH 9) and filtered. The organic phase is evaporated and the remaining aqueous phase is partitioned with dichloromethane. The organic phase is concentrated and taken up in acetone. The residue is oxidized, diluted with water and partitioned with dichloromethane. This extract is then taken through a series of clean-up steps prior to derivatization through refluxing with trifluoroacetic anhydride and trifluoroethanol. The analytes are partitioned with toluene and determined by GC/MS. Mean recoveries for analytes determined by the method are: $84.7 \pm 12.7\%$ for DCVA, $92.9 \pm 17\%$ for 3-PBA, and $97.2 \pm 15.6\%$ for 3-phenoxybenzoic acid.

Results

Results from the analysis of storage stability studies are given below in Table 1. Values in the table are from duplicate samples analyzed and the results averaged. All values have been corrected for recoveries less than 100%. Residues do not decline significantly for DCVA and 3-PBA in any of the matrices (racs) tested over the 36 month period stored at -20°C . Declines of up to 25% were seen in apples and peanut meats for 3-phenoxybenzoic acid; the metabolite was otherwise stable in the other racs tested.

Table 1. Residues of DCVA, 3-PBA and 3-phenoxybenzoic acid (3-PBAcid) in ppm in Various Racs Stored at -20°C and Analyzed Periodically over a 36-Month Period.

Chemical	0 Months	3 Months	12 Months	24 Months	36 Months
Residues in Tobacco (ppm)					
DCVA	0.098	0.089	0.086	0.086	0.096
3-PBAlc	0.109	0.133	0.094	0.093	0.096
3-PBAcid	0.107	0.102	0.090	0.095	0.090
Residues in Apples (ppm)					
DCVA	0.104	0.096	0.068	0.067	0.087
3-PBAlc	0.106	0.106	0.080	0.078	0.094
3-PBAcid	0.091	0.120	0.076	0.085	0.066

Chemical	0 Months	3 Months	12 Months	24 Months	36 Months
Residues in Cabbage (ppm)					
DCVA	0.102	0.119	0.094	0.089	0.086
3-PBAIc	0.103	0.103	0.093	0.085	0.091
3-PBAcid	0.113	0.101	0.085	0.065	0.092
Residues in Corn Fodder (ppm)					
DCVA	0.103	0.085	0.083	0.081	0.072
3-PBAIc	0.102	0.081	0.086	0.089	0.078
3-PBAcid	0.099	0.089	0.092	0.092	0.081
Residues in Corn Forage (ppm)					
DCVA	0.098	0.089	0.097	0.098	0.094
3-PBAIc	0.113	0.098	0.098	0.113	0.088
3-PBAcid	0.091	0.109	0.107	0.098	0.086
Residues in Cottonseed (ppm)					
DCVA	0.100	0.092	0.105	0.092	0.091
3-PBAIc	0.100	0.089	0.091	0.080	0.090
3-PBAcid	0.088	0.113	0.089	0.107	0.098
Residues in Lettuce (ppm)					
DCVA	0.089	0.098	0.105	0.100	0.099
3-PBAIc	0.108	0.103	0.093	0.096	0.105
3-PBAcid	0.103	0.116	0.085	0.083	0.093
Residues in Peanut Hulls (ppm)					
DCVA	0.099	0.085	0.074	0.088	0.080
3-PBAIc	0.101	0.105	0.061	0.108	0.075
3-PBAcid	0.100	0.091	0.096	0.092	0.092
Residues in Peanut Meats (ppm)					
DCVA	0.090	0.098	0.076	0.077	0.097
3-PBAIc	0.090	0.119	0.073	0.089	0.127
3-PBAcid	0.092	0.096	0.067	0.072	0.065

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Chemical	0 Months	3 Months	12 Months	EPA SERIES 361	
				24 Months	36 Months
Residues in Sorghum Grain (ppm)					
DCVA	0.105	0.092	0.095	0.095	0.084
3-PBAIc	0.111	0.100	0.084	0.105	0.082
3-PBAcid	0.104	0.082	0.099	0.095	0.083
Residues in Soybeans (ppm)					
DCVA	0.105	0.089	0.090	0.079	0.079
3-PBAIc	0.106	0.097	0.091	0.093	0.081
3-PBAcid	0.098	0.100	0.100	0.096	0.079
Residues in Sugar Beets (ppm)					
DCVA	0.091	0.096	0.099	0.098	0.090
3-PBAIc	0.099	0.116	0.096	0.093	0.092
3-PBAcid	0.101	0.112	0.090	0.084	0.102
Residues in Tomatoes (ppm)					
DCVA	0.100	0.095	0.076	0.080	0.091
3-PBAIc	0.099	0.092	0.079	0.093	0.101
3-PBAcid	0.109	0.069	0.077	0.072	0.094

cc: RF, SF, List B File, Circ., C. Eiden
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