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

AUG 19 1987

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: EPA Reg. No. 464-448. Chlorpyrifos Reregistration. Evaluation of Residue Data and Analytical Methods to Support Separate Tolerances for Chlorpyrifos and its metabolite 3,5,6-Trichloro-2-pyridinol for Cabbage, Cottonseed, and Strawberry. MIRD Nos. 401313-01, 401313-02, and 401313-03. RCB No. 2124.

FROM : Sami Malak, Ph.D., Chemist Sami Malak
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TO : Dennis Edwards, PM #12
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THRU : P. V. Errico, Section Head P. V. Errico
Tolerance Petition Section III
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Dow Chemical Company submitted residue data and analytical methods requesting maximum separate levels of chlorpyrifos for the tolerances currently established for these crops under 40CFR§180.342. Tolerances for chlorpyrifos in which the maximum level of chlorpyrifos, per se, is separately stated have been approved by RCB in connection with PP#3F2884 (memo of K. Arne, 9/8/87). The existing tolerances under 40CFR§180.342 and those approved by RCB are stated below:

Crop	PP No.	Established Tolerances	Approved Tolerances
Cabbage[1/]	7E2010	2 ppm (of which no more than 1 ppm is chlorpyrifos)	2 ppm (of which no more than 1 ppm is chlorpyrifos)
Cottonseed	6F1786	0.5 ppm	0.5 ppm (of which no more than 0.2 ppm is chlorpyrifos)
Strawberry	OF2283	0.5 ppm	0.5 ppm (of which no more than 0.2 ppm is chlorpyrifos)

1/ Tolerance is established for vegetables, leafy, Brassica (cole).

Permanent tolerances are currecntly established under 40CFR§180.342 for the combined residues of the insecticide chlorpyrifos [O,O-diethyl O-(3,5 6-trichloro-2-pyridyl) phosphorothioate] and its metabolite 3,5,6-trichloro-2-pyridinol in or on several raw agricultural commodities at levels from 0.05 to 15 ppm including 0.5 ppm for cottonseed and strawberry and 2 ppm (of which no more than 1 ppm is chlorpyrifos) for vegetables, leafy, Brassica (cole). Also, food/feed additive tolerances are currently established for the combined residues of the insecticide chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate] and its metabolite 3,5,6-trichloro-2-pyridinol in or on several commodities at levels from 0.05 to 15 ppm (21CFR §193.85 and §561.98).

The manufacturing processes of chlorpyrifos are described in Appendix A of the Chlorpyrifos Registration Standard , dated 1/25/84 [redacted] We do not foresee any residue problems in the subject crops with regard to impurities.

The formulation used on cabbage, cotton and strawberry is Lorsban 4E insecticide (EPA Reg. No. 464-448), an emulsifiable concentrate containing 40.7% chlorpyrifos, equivalent to

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4 lb act/gallon. All inerts are cleared under 40CFR§180. 1001 (see also PP#6F1777).

[redacted]

As per J. Akerman memo of 9/16/86, review of the inerts clearance for formulations is the purview of the Registration Division.

Registered Uses

Registered uses on cabbage, cotton, and strawberry are discussed in connection with PP#7E2010 for cabbage, PP# 6F1786 for cotton, and PP#OF2283 for strawberry. These uses are also summarized by K. Arne in PP#3F2884, 9/8/83.

The use on cabbage stipulates a maximum of two applications of Lorsban 4E, each at 1.6 fl oz act/1000 linear foot of row. There is a 30-day PHI.

The use on cotton would allow multiple applications, each at 1 lb act/A of Lorsban 4E with a 14-day PHI.

The use on strawberry is limited to prebloom applications of Lorsban 4E at 1 lb act/A/application with a 21-day PHI.

Nature of Residues

The metabolism of chlorpyrifos in plants has been discussed in several petitions from which we have concluded that the residues of concern in plants consist of the parent compound, chlorpyrifos, and its metabolite 3,5,6-trichlor-2-pyridinol or TCP as expressed in 40CFR1180.342 (see also PP#'s 6F1777, 1F2620, 3F2778, 4F2999, 4F3008, 4F3062, and the Chlorpyrifos Registration Standard).

The metabolism of chlorpyrifos in animals is not adequately understood. Additional animal metabolism studies in ruminants and poultry were requested in connection with the Chlorpyrifos Registration Standard (1/25/84). However,

for the purpose of this review, we are not raising any questions as to the need for the animal metabolism studies which should be addressed in connection with the Chlorpyrifos Registration Standard.

Analytial Methods

The registrant submitted two methods for residue determination of chlorpyrifos and TCP in plants.

Dow's Method ACR84.4 for Cabbage and Strawberry

The method entitled "Determination of Residues of Chlorpyrifos and 3,5,6-Trichloro-2-pyridinol in or on Cabbage Following Two Applications of Lorsban 4E Insecticide." The method is essentially the same as that in PAM II, Method II. The method, identified as Dow's ACR84.4 was previously submitted and discussed in connection with PP#4F3062 and 6F3357. Method sensitivity is reported at 0.05 ppm for TCP and 0.01 ppm for chlorpyrifos, per se.

For chlorpyrifos determination, method ACR84.4 involves extracting cabbage samples in acetone. The extracts are concentrated and diluted with water. The aqueous solution is then passed through a C_{18} Sep-Pak via compressed air. Chlorpyrifos is then eluted from the Sep-Pak with methanol then extracted with hexane and chlorpyrifos is determined using GC equipped with a flame photometric detector.

The efficiency of the method was determined by fortifying control cabbage samples with chlorpyrifos at 0.01 and 0.02 ppm and strawberry at 0.01 to 10 ppm. recoveries ranged from 92 to 113%, averaging 100% for cabbage and from 76 to 101%, averaging 86% for strawberry.

Method ACR84.4 was also used to determine TCP in cabbage and strawberry. Any chlorpyrifos present was hydrolyzed to TCP so that the analysis is for total TCP. The amount of TCP is given as the difference between the total amount detrermined here and the amount of TCP equivalent to the chlorpyrifos determined by the above procedure.

To determine total TCP, samples are extracted in methanolic sodium hydroxide. The alcohol is evaporated and the residue is taken up in hydrochloric acid and forced through a C_{18} Sep-Pak. The TCP is eluted with methanol into benzene and sodium bicarbonate. The mixture is

centrifuged and the bicarbonate is drawn off and acidified with concentrated HCl. The acidified solution is partitioned with benzene. An aliquot of the benzene is then treated with BSA [N,O-bis(trimethylsilyl)acetamide] to form the trimethyl derivative and diluted with benzene. The TCP silyl derivative is then determined by GC using electron capture detection.

The efficiency of the method was determined by fortifying control cabbage samples with TCP at 0.05 to 0.1 ppm and strawberry at 0.05 to 5 ppm. Recoveries ranged from 81 to 103%, averaging 95% for cabbage; and from 76 to 104%, averaging 92% for strawberries.

Dow's Method ACR73.5.S1/ACR71.19R.S6 for Cottonseed

The methodology entitled "Determination of Chlorpyrifos and 3,5,6-Trichloro-2-Pyridinol in or on Cottonseed Following Five Foliar Applications of Lorsban 4E." The method is essentially the same as that of Method II, PAM II.

The first part of the method, ACR73.5.S1, detrmines chlorpyrifos, per se, in/on cottonseed. In this method, chlorpyrifos is extracted from cottonseed with acetone. The acetone is evaporated, diluted with water and the aqueous residue is partitioned with hexane. The hexane solution is partitioned against acetonitrile and the acetonitrile is evaporated. The residue is then taken up in hexane and cleaned up on a silica gel column. The hexane eluate is concentrated to dryness. The residue is then dissolved in acetone and the chlorpyrifos is determined by GC using flame photometric detection. Method sensitivity is reported at 0.01 ppm.

The efficiency of the method was determined by fortifying control samples with chlorpyrifos at 0.01 to 1 ppm. Recoveries ranged from 76 to 96%, averaging 86%.

The second part of the methodology, ACR71.19R.S6, determines TCP in/on cottonseed. In this method, cottonseed samples are heated in methanolic sodium hydroxide. This method determines total pyridinol since all of the TCP and chlorpyrifos are converted to the sodium salt of pyridinol. The TCP is then determined by difference between the total pyridinol found on hydrolysis and the pyridinol equivalents from the chlorpyrifos by method ACR73.5.S1. After heating,

the sample is blended, filtered and brought to a known volume. An aliquot is taken with water, sodium chloride and benzene. The methanol/water aliquot is acidified and shaken with benzene. The benzene is removed and placed on an acidified alumina column for clean-up. The compound is then eluted from the column with a diethyl ether, pH 6.5 buffer solution. The other eluate is partitioned with sodium bicarbonate. The sodium bicarbonate solution is taken with benzene for additional clean-up, and the benzene is discarded. The bicarbonate solution is then acidified and back-partitioned with benzene. The benzene is brought to a known volume and an aliquot is tretaed with BSA [N,O-bis(trimethylsilyl) acetamide] to form the pyridinol trimethyl derivative which is then determined by GC using electron capture detection.

The efficiency of the method was determined by fortifying control samples with TCP at 0.05 to 1.0 ppm. Recoveries ranged from 71 to 111%, averaging 87%.

Sample chromatograms are included.

Adequate analytical methods are available for residue determination of chlorpyrifos and its metabolite TCP in/on plants. Dow's methods ACR84.4 for chlorpyrifos and TCP; and ACR73.5.S1 for chlorpyrifos/ACR71.19R.S6 for TCP are essentially the same as Method II of PAM II that may be used for enforcement.

Storage Stability

Storage stability studies for residues of chlorpyrifos in/on several plant and animal commodities are discussed in connection with the Chlorpyrifos Registration Standard (1/25/84). RCB had previously concluded that residues of chlorpyrifos and TCP are stable in plant and animal samples for periods of up to 23 months when stored at subfreezing temperatures (-20°C).

Residue Data

Cabbage- Data submitted reflect four field tests from Zellwood, Florida in which Lorsban 4E was applied at planting and a second application as directed band 30 days post plant, each at 1.4 oz act/1000 feet of row. Samples were taken at maturity, 90 days after planting, frozen in dry ice until analyzed 20 days later.

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Chlorpyrifos and TCP residues were reported separately at 95 day-PHI. No chlorpyrifos (<0.01 ppm) or TCP (<0.05 ppm) were detectable in any of the samples.

Strawberry- Data submitted reflect 12 field trials from California, Idaho, and Oregon in which Lorsban 4E was applied preplant using 1 lb act/A in CA and 2 lb act/A in ID and OR. This was followed by one foliar application in CA and 2 foliar applications in ID and OR, each at 1 lb act/A. Samples were harvested, frozen on dry ice until analyzed 60 days later.

Chlorpyrifos and TCP residues were reported separately. Corrected values for average control and recovery ranged from non-detectable (<0.01 ppm for chlorpyrifos and <0.05 ppm for TCP) to a maximum of 0.08 ppm for chlorpyrifos and 0.09 ppm for TCP. The maximum combined residues in strawberry was 0.13 ppm (0.08 ppm chlorpyrifos and 0.05 ppm pyridinol). All residue values reflect 21 day PHI. The combined residue is less than the established tolerance of 0.05 ppm for strawberry.

Cottonseed- Data submitted reflect four field tests from Keneson, Fresno County, California in which Lorsban 4E was applied 5 times, each at 1 lb act/A beginning at four months after planting to 14 days before harvest (180 days from planting to harvest). Samples were collected, frozen in dry ice until analyzed 68 days later.

Chlorpyrifos and TCP residues were reported separately. Corrected values for average control and recovery ranged from 0.12 to 0.2 ppm for chlorpyrifos and from 0.12 to 0.21 ppm for TCP. The maximum combined residues in cottonseed was 0.37 ppm (0.18 ppm chlorpyrifos plus 0.19 ppm pyridinol). The combined residue is less than the established tolernce of 0.5 ppm.

We conclude that the submitted residue data support RCB's previously recommended tolerances for cabbage, cottonseed, and strawberry as follows (see PP#3F2884, K. Arne, 9/8/87):

Cabbage 2 ppm of which no more than 1 ppm is chlorpyrifos.

Cottonseed 0.5 ppm of which no more than 0.2 ppm is chlorpyrifos.

Strawberry 0.5 ppm of which no more than 0.2 ppm is chlorpyrifos.

Incorporaton of these tolernaces in 40CFR§180.342 should be done in a manner similar to those of carbofuran under §180.254.

Conclusions and Recommendation

The submitted residue data support RCB's previously recommended tolerances for cabbage, cottonseed, and strawberry as follows (see PP#3F2884, K. Arne, 9/8/87):

Cabbage 2 ppm of which no more than 1 ppm is chlorpyrifos.

Cottonseed 0.5 ppm of which no more than 0.2 ppm is chlorpyrifos.

Strawberry 0.5 ppm of which no more than 0.2 ppm is chlorpyrifos.

Note to PM:

Incorporaton of these tolernaces in 40CFR§180.342 should be done in manner similar to those of carbofuran under §180.254.

cc: R.F., Circu, S. Malak, S.F. (chlorpyrifos), PP#1F2507, PP#3F2884. TOX, EAB, EEB, FDA, and PMSD/ISB.

RDI: P.V. Errico: 8/17/87: R.D. Schmitt: 8/17/87
TS-769:RCB:RM:810:CM#2:S.Malak:X557-4379:6/25/87