1-15-81 Petition File

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PP#1G2438/FAP#1H5284. Chlorpyrifos on wheat. Evaluation of analytical methods and residue data.

Lynn M. Bradley, Chemist
Residue Chemistry Branch, HED (TS-769)

Jay Ellenberger, PM Team 12
Registration Division (TS-767)
and
Toxicology Branch, HED (TS-769)
Hazard Evaluation Division

Thru: Robert J. Hummel, Head, Special Review Section
Residue Chemistry Branch (TS-769)

Richard D. Schmitt, Deputy Branch Chief
Residue Chemistry Branch (TS-769)

Charles Trichilo, Chief
Residue Chemistry Branch (TS-769)

Dow Chemical Company is requesting temporary tolerances for combined residues of the insecticide chlorpyrifos [0,0-diethyl0-(3,5,6-trichloro-2-pyridyl)-phosphorothioate] and its metabolite 3,5,6-trichloro-2-pyridinol in or on the r.a.c.s wheat at 0.15 ppm, wheat straw at 1.5 ppm and milling fractions (except flour) of wheat at 0.5 ppm.

Tolerances are established on various r.a.c.s at levels ranging from 0.05 to 2 ppm, and on meat, milk, poultry and eggs at levels of 0.01 to 1.5 ppm (40 CFR 180.342).

RCB has recommended for a tolerance on nectarines(PP#9E2215) at 0.05 ppm.

Petitions pending or in reject status are 6F1830(sorghum), 8E2092(tomatoes), 9F2193(peanuts), 9G2168(citrus), 9F2221 (various), 0F2281(alfalfa), 9F2270 (soybeans, goats and sheep), 0E2283 (strawberries), 0E2411(turnips),0E2412 (Chinese Cabbage) and 0E2372(mint).

Two EUPs are requested in conjunction with these temporary tolerances. One is for the states of Illinois and Texas and is accompanied by a crop destruct clause. The other is for the states of Kansas, Minnesota and South Dakota. Not more than 600 acres(200 per state) will be treated with up to 900 lbs. active chlorpyrifos.

CONCLUSIONS

1. For the purposes of this temporary tolerance only, we consider the metabolism of chlorpyrifos in plants and animals to be adequately understood. For any future permanent tolerances, the studies requested in PP#0F2270 will be required.

2. Adequate analytical methodology is available to enforce the proposed temporary tolerance for residues of chlorpyrifos and its metabolite, TCP.

3a. The proposed temporary tolerance for wheat grain is not adequate. In order to determine an appropriate temporary tolerance level, we will require additional residue data reflecting the maximum proposed use (1 application of 0.5 lb a.i./A followed by a second at 1 lb a.i./A and a 14 day PHI).

3b. The proposed temporary tolerance for wheat straw is not adequate. Additional residue data (see Conclusion 3a) will be required.

3c. Residue data and an appropriate tolerance proposal for wheat forage should be submitted.

3d. The proposed temporary food additive tolerance for milling and baking fractions (except flour) of wheat is not adequate. An appropriate level for milling fractions will be 3X that for the grain.

5. We are unable to reach a conclusion regarding secondary residues in meat, milk, poultry and eggs until such time as appropriate levels are established for grain, forage, straw and milling fractions.

RECOMMENDATIONS

For the reasons cited in Conclusions 3a,3b,3c,3d and 5, we recommend against the proposed temporary tolerances. Revised Sections B and F should be submitted.

Petitioner should be advised that for any permanent tolerances on wheat, the metabolism questions raised in PP#0F2270 should be resolved.

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DETAILED CONSIDERATIONS

Manufacture and Formulation

Lorsban 4E, 4 lb active chlorpyrifos per gallon emulsifiable concentrate, is the formulation proposed for use. All inert ingredients in this registered formulation are cleared under 40 CFR 180.1001.

The manufacturing process was described in our review of PP#4F1455 (A. Smith, 6/3/74). None of the impurities in the technical material are expected to present a residue problem.

Proposed Use

Apply 0.25 - 1.0 lb active chlorpyrifos per acre as broadcast foliar spray, using aerial or ground equipment. Use ground equipment only in the fall to newly planted winter wheat--aerial applications may be used at any time.

Do not apply more than 1.5 lb active per acre per season, and do not apply within 14 days of harvest. Do not allow livestock to graze in treated fields nor feed treated straw to meat or dairy animals within 14 days of application.

Nature of the Residue

No new metabolism data are submitted with this petition. The available metabolism data was first reviewed in PP#3F1306 and PP#4F1445.

Until recently (PP#0F2270, E. M. K. Leovey, 4/29/80), the metabolism of chlorpyrifos in plants and animals was considered to be adequately defined. In plants, chlorpyrifos is absorbed and translocated to a limited extent from the leaf surface. Absorption probably occurs after photodecomposition. The parent compound is hydrolyzed to ethyl 3,5,6-trichloro-2pyridyl phosphate; 3,5,6-trichloro-2-pyridyl phosphate; 3,5,6trichloro-2-pyridinol (known as TCP and included in the regulated residue) and material postulated to be a TCP conjugate. We have now requested that the unidentified material in the available bean metabolism study be further characterized.

For the purposes of this temporary tolerance, we consider the metabolism plants to be adequately defined. For any permanent tolerance on wheat, the metabolic studies on chlorpyrifos in plants which were requested in connection with PP#0F2270 will be required.

Likewise, questions have been raised concerning the animal metablism. We have previously concluded that chlorpyrifos is metabolized by oxidation and hydrolysis to phosphoric acid-type compounds and TCP which are further metabolized to CO_2. There are no large animal studies available in our files, but published studies indicate that other metabolites may be present. (See the review of Leovey, 4/29/80, PP#OF2270.)

For the purposes of this temporary tolerance, we consider the metabolism of chlorpyrifos is adequately defined. The petitioner should be advised that for any permanent tolerance on wheat, the large animal metabolism questions which are outstanding will have to be resolved. Furthermore, if any additional plant metabolites are judged to be significant and in need of regulation, animal metabolism studies for these compounds may be required for any permanent tolerances.

Analytical Method

Residues of chlorpyrifos are determined in wheat, straw and milling and baking fractions by method ACR 73.5.S1, which is similar to the method published in PAM II and has been accepted for enforcement purposes in several other petitions.

The sample is blended with acetone and the extract filtered. The filtrate is evaporated to remove acetone and the aqueous residue partitioned into hexane, then hexane: acetonitrile. After silica gel chromatography, the solvents are removed and the residue taken up in acetone. Quantitation is by GC using a flame photometric detector which is highly specific for phosphorus.

In grain, control values range from 0.001 to 0.008 ppm, and recoveries at fortification levels of 0.01 to 1.0 ppm were 80 to 121%. In straw, controls were 0.004 to 0.022 ppm, and recoveries at fortification levels of 0.01 to 2.0 ppm were 78 to 110%. For the milling and baking fraction (bran, flour, break shorts, reduction shorts, red dog and bread), control values were 0.002 ppm (bread) to 0.02 ppm (bran); recoveries at fortification levels of 0.05 and 2.0 ppm were 66 to 88%.

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Residues of the 3,5,6-trichloropyridinol (TCP) metabolite are determined by difference--all residues are converted to TCP by heating the commodity in methanolic NaOH and the residues of parent determined by an alternate method. After conversion to TCP, the extract is filtered, diluted with water and made saline, then partitioned with benzene which is discarded. The remaining aqueous solution is made acidic and re-extracted with benzene. The benzene phase is chromatographed on acidic alumina in diethyl ether and the ether eluate partitioned with $NaHCO_3$ which is acidified and back-partitioned with benzene. The pyridinol is converted th the trimethylsilyl derivative and determined by GC using an electron capture detector.

For grain, control values were 0.005 to 0.010 ppm and recoveries at fortification levels of 0.05 to 1.0 ppm were 66 to 82%. For straw control values were 0.008 to 0.034 ppm and recoveries at fortification levels of 0.05 to 2.0 ppm were 72 to 85%. For the baking and milling fractions (as above), controls were 0.007 to 0.031 ppm and recoveries at fortification levels of 0.05 and 2.0 were 70 to 86%.

We conclude that adequate analytical methodology is available to enforce the proposed temporary tolerance for combined residues of chlorpyrifos and TCP.

Residue Data

Data from 6 residue studies in 5 states are submitted. In each study, 3 applications of 0.5 lb a.i./A chlorpyrifos were made, and PHI's range from 14 to 17 days. The time interval between applications ranged from 9 to 19 days; three studies used spring wheat and three studies used winter wheat (insecticide being applied in late spring or early summer), and both aerial and ground applications were made. Data for straw are not reported for one of the studies used for milling fractions.

In the grain, maximum residues of chlorpyrifos ranged from 0.02 to 0.55 ppm and maximum residues of TCP ranged from ND(<0.05) to 0.25 ppm. In the straw, maximum residues of chlorpyrifos ranged from 0.08 to 1.7 ppm and maximum residues of TCP ranged from 0.06 to 0.92 ppm.

Obviously, the proposed tolerances of 0.15 ppm for wheat and 1.5 ppm for straw are not adequate. The residue studies submitted reflect a reasonable interpretation of the proposed use, and indicate that combined residue levels of the parent and TCP will exceed the levels proposed for temporary tolerances. We anticipate that actual residue levels could be even higher, since Section B indicates that up to 1.0 lb ai/A may be applied with a 14 day PHI.

In order to determine the appropriate tolerance level, we will require additional residue data reflecting the maximum proposed use (one application at 0.5 lb a.i./A followed by a second at 1 lb a.i./A and a 14 day PHI).

Also, residue data and a tolerance proposal for wheat forage will be required.

The residue study which was used to produce milling and baking fractions had the maximum residue levels in grain (0.55 ppm). The majority of the residue remained in the outer portion of the wheat berry, while the endosperm had minimal residues.

Fraction	Chlorpyrifos(ppm)	TCP (ppm)
Bran	1.5	0.63
Flour	0.08	0.06
Break Shorts	1.0	0.42
Reduction Shorts	1.4	0.62
Red Dog	0.47	0.15
Bread	0.06	<0.05

The proposed temporary food additive tolerance for milling fractions is not adequate. The concentration observed in the bran fraction is ca. 3X, so an appropriate temporary food additive tolerance level for milling fractions (except flour) of wheat would be 3 times the level for grain (when established).

Meat, Milk, Poultry and Eggs

No new feeding studies are presented in this petition.

Existing tolerances are 0.1 ppm for the meat, fat, and meat byproducts of goats, hogs, horses and sheep; 1.5 ppm for the meat, fat and meat by-products of cattle and 0.25 ppm in milk fat (representing 0.01 ppm in whole milk).

In PP#3F1306, it was reported that no chlorpyrifos residues were found in whole milk after dairy cattle had been fed chlorpyrifos at levels of 1,3 and 10 ppm in the diet for 14 days. Chlorpyrifos residues of 0.02 ppm were found in whole milk after a 30 ppm feeding level. At the 1 and 3 ppm feeding levels, the maximum amounts of residues were 0.04 and 0.15 ppm, respectively. After withdrawal periods of 1-5 days, neither the milk nor the cream contained any detectable residues.

Beef cattle were fed chlorpyrifos in the daily diets at levels of 3, 10, 30 and 100 ppm for 30 days. The feeding level of 3 ppm gave maximum 0.16-0.23 ppm residues in liver, and the 10 ppm level gave maximum residues of 0.5 ppm in kidney. The 30 ppm level gave a maximum residue of 1.7 ppm in liver. At the 100 ppm level, a maximum of 5 ppm was found in beef fat; this decreased to 0.04 ppm 35 days after cessation of feeding. Apparently, residues of TCP were not analyzed for.

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Pigs were fed chlorpyrifos in the daily diets at 0.3, 1, 3 and 10 ppm for 30 days. Residues (parent plus TCP) were not detected in any tissues at the 1 ppm feeding level. The 3 and 10 ppm levels gave maximum residue values of 0.08 and 0.3 ppm in liver. No residues were found in any tissues 21 days after cessation of feeding.

Feed items are bean vines (1 ppm) at 35% of the diet, corn grain (0.1 ppm) at 80% of the diet, wheat grain at 50% of the diet, wheat bran at 25% of the diet, wheat forage at 70% of the diet and wheat straw at 10% of the diet. Until appropriate tolerance levels are established for wheat grain, forage, bran and straw, we are unable to determine the level of chlorpyrifos in the diet of livestock and thus we are unable to determine whether existing meat and milk tolerances are adequate.

Existing tolerances are 0.01 ppm for eggs and the meat, fat and meat by-products of poultry (except turkeys), and 0.2 ppm for the meat, fat and meat by-products of turkeys.

Laying hens were fed chlorpyrifos in the daily diets at levels of 0.3, 1, 3 and 10 ppm for 30 days. No residues were detected in eggs of hens fed at the 10 ppm level. Residues in tissues at the 0.3, 1, 3 and 10 ppm feeding levels were ND(<0.01 ppm), 0.1, 0.2 and 0.8 ppm, respectively.

Poultry feed items are beans (0.05 ppm) at 15% of the diet, corn grain (0.1 ppm) at 70% of the diet, wheat grain at 70% of the diet and wheat bran at 10% of the diet. We are unable to determine what residue levels of chlorpyrifos in the diet of poultry might be until such time as appropriate tolerance levels for wheat grain and bran are established. Thus we are unable to make a final conclusion as to the adequacy of the established tolerances for poultry and eggs.

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