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

JUL 8 1982

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#2E2644. Chlorpyrifos in or on Asparagus

FROM: R. W. Storherr, Chemist
RCB, HED (TS-769) R.W.S.

THRU: Charles L. Trichilo, Chief
RCB, HED (TS-769)

TO: Clinton L. Fletcher (PM-43)
Registration Division (TS-767)

and

Toxicology Branch
Hazard Evaluation Division (TS-769)

Dr. R. H. Kupelian on behalf of the IR-4 Technical Committee and the Agricultural Experiment Station of Washington requests the establishment of a 2.0 ppm tolerance for the combined residues of chlorpyrifos and its TCP metabolite in or on asparagus.

Permanent tolerances have been established for residues of chlorpyrifos and its metabolite, 3,5,6-trichloro-2-pyridinol (TCP), at levels ranging from 0.01 ppm in eggs to 15 ppm in peanut hulls (40 CFR 180.342).

A letter of authorization from Robert F. Bischoff, Product Registration Manager, January 6, 1982, allows EPA to use all relevant Dow data on chlorpyrifos in support of this petition.

Conclusions

1. The metabolism and degradation of chlorpyrifos in plants and animals has been adequately studied and described.

2. Analytical methods (GLC) for both chlorpyrifos and TCP are available for enforcement purposes.

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3. The residue data for asparagus are limited. The 1977 residue samples were stored for an extended period of time and are of questionable value. Analyses were for chlorpyrifos per se.

   The 1979 data reflect analysis for the residue, TCP. When residues are calculated in terms of chlorpyrifos, the data at the 1X application rate indicate that residues will approach the proposed tolerance. The data from the 2X rate, when adjusted for dosage, indicate that residues on asparagus will exceed the proposed tolerance.

   The data are limited in scope and do not present a clear residue picture. Additional residue data reflecting the maximum proposed use should be submitted.

4. Since asparagus is not likely to be used as an animal feed, we expect no problem of secondary residues in meat, milk, poultry, and eggs from the proposed use.

Recommendation

We recommend against the proposed tolerance for chlorpyrifos in or on asparagus because of Conclusion 3.

Detailed Considerations

Lorsban 4E Insecticide (EPA Registration No. 464-448) is formulated by Dow Chemical Company to contain 4 lbs. a.i. chlorpyrifos per gallon emulsifible concentrate. Lorsban 4E consists of 40.7% chlorpyrifos [0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate], 22.8% aromatic petroleum derivatives solvent, and 36.5% inert ingredients. All inert ingredients have been exempted from the requirements of a tolerance under Section 180.1001(c).

The manufacturing process and technical purities have been described previously (PP# 4F1445 and PP# 6F71673). There will be no residue problems resulting from the impurities in technical chlorpyrifos.

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Proposed Use

Chlorpyrifos formulated as Lorsban 4E Insecticide is to be used for the control of cutworms on asparagus in the Pacific Northwest Region. The maximum rate of application is 2 pts. (1 lb. a.i./A) with only one application per season.

The postharvest interval is 1 day.

Lorsban 4E insecticide is applied as a band spray usually when the soil is moist and the cutworms are near the ground surface.

Nature of the Residue

No metabolism data were submitted with this petition on asparagus. The metabolism of radiolabeled chlorpyrifos (^{36}Cl and ^{14}C labels) was studied on beans and corn (J. Agr. Food Chem. 15, 127 (1967)). It was determined that 80% of the dosage applied to surface areas was lost through volatility during the first 3 days. The remaining dosage stayed at the site of application and showed little or no translocation (only 1-2%). The small amount of products translocated (1-2%) were the degradation products such as 3,5,6-trichloro-2-pyrdinol (TCP). In this study, translocation of chlorpyrifos by either root or leaf absorption was found to be insignificant. The half-life for ^{14}C-labeled chlorpyrifos is 80-90 days; it is hydrolyzed to ^{14}C-labeled TCP only slowly. The uptake of TCP by the roots is dependent upon soil pH. At pH 6 or below free pyridinol will be present but not absorbed; at pH 7 or above, TCP will be present as a water-soluble salt and may be absorbed.

The nature of the plant and animal residues have been discussed previously in PP# 3F1306 and PP# 4F1445. The products of concern in plants is the parent compound, chlorpyrifos, and the metabolite TCP. The oxygen analog has not been described as being present in any residue.

The metabolism of chlorpyrifos in animals (rats, cows, pigs, chickens) occurs through oxidation and hydrolysis to water-soluble phosphoric acid derivatives which are then excreted via the urine. As such, the liver and kidney show mainly TCP residues while the fat may show chlorpyrifos residues. As with plants, the products of concern in animals are the parent and TCP. The oxygen analog derivative has not been found and is of no concern.

The nature of the residue in plants and animals has been adequately studied and reported.

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Analytical Method

There are two analytical methods (GLC), one for the 3,5,6-trichloro-2-pyridinol (TCP) metabolite, and one for the parent compound, chlorpyrifos:

TCP Method - This is the Dow Chemical Company Method ACR 71.19R, dated September 27, 1973, modified for frozen asparagus spears. For this, chopped asparagus is refluxed with methanol and NaOH and the liquid decanted and saved. This reflux and decanting is repeated two more times, the decantates combined, and the volume measured. A 5g sample aliquot is removed, diluted with water and extracted with benzene several times. The benzene washes are discarded. The aqueous layer is refluxed with HCl and NaCl and partitioned 3 times with benzene. The benzene extracts are combined, concentrated to a small volume, and placed on a Florisil column. TCP is eluted from Florisil with ethyl ether (previously treated at pH 6.5) then partitioned into bicarbonate solution, made acidic with HCl, and again extracted into benzene. The TCP silyl derivative is prepared directly on this extract using N,O-bis-(trimethyl silyl)acetamide (BSA). This final solution is made to a definite volume and TCP silyl derivative determined by GLC-EC using a 5% DC-200 Gas Chrom Q column at 150°C. Sensitivity is 0.05 ppm.

Chlorpyrifos Method - Chopped asparagus spears are blended with 0.1N HCl in acetone and ethyl acetate and refluxed 20 minutes and decanted (reflux and decanting are repeated twice more). The decantates are combined, measured, and a 10 g aliquot removed and concentrated to 1 ml volume. This sample concentrate is then cleaned up by sweep co-distillation at 200°C.

Chlorpyrifos is analyzed by GLC using the flame-photodetector (FPD). The GLC column is 5% DC-200 plus 7.5% QF-1 on Gas Chrom Q at 200°C. The method sensitivity is 0.01 ppm chlorpyrifos. All control crops showed less than 0.01 ppm chlorpyrifos. Recoveries of fortifications of 0.01, 0.05, 0.50, and 1.00 ppm were 90, 86, 90, and 87%, respectively. Storage fortifications at 0.01, 0.05, and 1.0 ppm for 5 months were 101, 100, and 99.4% respectively.

Residue Data

In 1977, asparagus plots in Washington State were treated with one application of Lorsban 4E Insecticide formulation

at rates of 0.75, 1.0, and 1.5 lb. ai./A. This represented 3/4, 1, and 1 1/2 times the maximum chlorpyrifos dosage of 1 lb. a.i./A. The samples were stored for approximately 1 1/2 years after harvest, then extracted and held in solution for one month prior to analysis. In the 1977 study, samples were analyzed only for chlorpyrifos. The maximum residues, 0.60 ppm, were found one day after treatment from the 1.0 and 1.5 lb. a.i./A dosages.

No samples were analyzed for 3,5,6-trichloro-2-pyridinol (TCP) in 1977-1978.

In 1979, asparagus was again treated with Lorsban 4E Insecticide in Washington State. This study was one application of 1, 1 1/2, and 2 lb. a.i. chlorpyrifos/A (1, 1 1/2, and 2X the maximum recommended dosage).

Instead of analyzing for chlorpyrifos, the petitioner analyzed for total TCP, net TCP, and TCP from chlorpyrifos (no data are reported on chlorpyrifos). The 1-day PHI residues, at the 1 lb. a.i./A rate, ranged from 0.64-0.97 ppm TCP. However, on converting these values to chlorpyrifos (= TCP/0.56), the residues range from 1.14-1.73 ppm chlorpyrifos at a 1-day PHI.

The TCP residues for the 1-day PHI 1 1/2 and 2 lbs. a.i./A rates, after conversion, show maximum chlorpyrifos of 3.00 and 5.28 ppm, respectively. A study of the data from the 1 lb. a.i./A rate over the 10-day PHI period shows:

PHI, Days	TCP Total ppm	Chlorpyrifos Total* ppm
0	ND	ND
1	0.64; 0.97	1.14; 1.73
2	0.09	0.16
3	0.11; 0.43	0.20; 0.76
7	0.41	0.73
8	0.62	1.10
10	0.86	1.53

ND - Not determined.
* From total TCP divided by 0.56.

From the above data, it is apparent that the residues from samples treated at the 1X rate are not declining significantly over the 10-day PHI duration. The 1-day and 10-day PHI have about the same ppm chlorpyrifos.

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Overall, the data are limited and the residue picture is unclear.

The residue data from 1977 are of questionable value because of the long sample storage period and these samples generally show lower residues than samples from the 1979 study involving shorter storage periods. In the 1979 studies, residues on asparagus treated at the 1X rate approach the proposed tolerance. Those data at the 2X rate, when adjusted for dosage, indicate that the proposed tolerance may be exceeded. Additional residue data reflecting the maximum proposed use are needed. TOX has indicated to us that they would be concerned about recommending for a tolerance higher than 2 ppm.

Meat, Milk, Poultry and Eggs

Because the proposed use involves no feed items, there is no problem of secondary residues in meat, milk, poultry and eggs. Even if parts of asparagus were to be used as a livestock feed, any secondary residues would be covered by the established meat, milk, poultry and egg tolerances.

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Chlorpyrifos PETITION PP# 2644

CCPR NO. 17 IC

Codex Status

/ / No Codex Proposal Step 6 or above

Residue (if Step 9): _____

Crop(s) Limit (mg/kg)

None (on asparagus)

Proposed U. S. Tolerances

2 ppm Chlorpyrifos in or on asparagus

Residue: Chlorpyrifos and its TCP metabolite

Crop(s) Tol. (ppm)

Asparagus 2

CANADIAN LIMIT

Residue: _____

Crop Limit (ppm)

None (on asparagus)

MEXICAN TOLERANCIA

Residue: _____

Crop Tolerancia (ppm)

None (on asparagus)

Notes:

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