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

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

JUN 8 1993

MEMORANDUM

SUBJECT: PP#3E2819. Chlorpyrifos in or on the crop group brassica leafy vegetables. Evaluation of residue data and analytical methodology.

FROM: Jesse E. Mayes, Chemist
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THRU: Charles L. Trichilo, Chief
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TO: Hoyt Jamerson, PM43
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and

Toxicology Branch
Hazard Evaluation Division (TS-769)

The IR-4 National Director and Assistant Coordinator of the IR-4 State Agricultural Experiment Station at Rutgers University, on behalf of the IR-4 Technical Committee and Agricultural Experiment Stations of Hawaii, Idaho, Michigan, New Jersey, Washington, Wisconsin, and the U.S. Department of Agriculture, requests that the established 2 ppm tolerance for combined residues of the pesticide chlorpyrifos (0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate and its metabolite 3,5,6-trichoro-2-pyridinol (TCP) in or on the raw agricultural commodities broccoli, brussels sprouts, cabbage, Chinese cabbage, and cauliflower be extended to include the crop group brassica leafy vegetables, which also include Chinese broccoli, broccoli raab, Savoy cabbage, collards, kale, kohlrabi, mustard greens and rape greens.

Tolerances have already been established for numerous raw commodities ranging up to 15 ppm in or on alfalfa hay.

These tolerances include meat and meat byproducts, poultry and poultry byproducts, milk and eggs.

Conclusions

1. The nature of the residue is adequately understood. The residue of concern is the parent compound and its metabolite 3,5,6-trichloro-2-pyridinol.

2. A satisfactory analytical method is available for enforcement purposes.

3a. The tolerance proposed for the crop grouping brassica leafy vegetables is inappropriate at this time. The only crop grouping scheme in effect at this time is for negligible crop tolerances (40 CFR 180.34(f)); the presently proposed tolerances are not negligible and this scheme does not apply. The recently proposed crop grouping which appeared in the Federal Register would apply to all crop group tolerances but has not yet been adopted.

3b. Residue data previously submitted and reviewed for already established tolerances are adequate to support a tolerance level of 2 ppm in or on Chinese broccoli, broccoli raab, kohlrabi and Savoy cabbage.

3c. Additional data, on at least mustard greens, are needed to support tolerances for the leafy vegetables, collards, kale, mustard greens and rape greens.

The residue study submitted on kale is inadequate in number to support a tolerance. While the available turnip green residue data are also supportive, additional residue data should be submitted for crops in this grouping which is to include collards, kale, mustard and rape.

3d. In conclusion, the available data are adequate to support a 2 ppm tolerance for Chinese broccoli, broccoli raab, kohlrabi and Savoy cabbage.

Additional residue data are needed for collards, kale, mustard and rape greens to support tolerances on these commodities.

4. Any secondary residues occurring in meat, milk, poultry or eggs would be covered by existing tolerances for these commodities.

5. The proposed tolerances are twice those involved Codex tolerances and include the metabolite TCP whereas Codex does not. It does not appear that these tolerances would be compatible.

Recommendations

We recommend that the tolerances not be established because of conclusions 3a, 3c and 3d. Additional data are needed for leafy vegetables which would reflect studies in representative growing regions and would reflect the proposed usage.

Based on data we have already reviewed (PP7E2010) we could recommend for establishment of tolerances of 2 ppm for Chinese broccoli, broccoli raab, kohlrabi and Savoy cabbage if these tolerances were proposed.

Detailed Considerations

Formulation

Two formulations are proposed for use: Lorsban® 4E (EPA Reg. No. 464-448) and Lorsban® 15G (EPA Reg. No. 464-523). The 4E, an emulsifiable concentrate, contains 41% active ingredient and the 15G, a granular formulation, contains 15% active ingredient. The inert ingredients in both formulations are cleared in 40 CFR 180.1001. The manufacturing process in both formulations has been discussed in earlier petitions (PP4F1445 and PP6F1673). The impurities are not expected to cause a residue problem.

Proposed Use

Chlorpyrifos is to be used to control root maggots in the listed crops. Both the 4E and the 15G are to be incorporated into the soil at planting of seeds. The 4E can also be applied to the base of transplants. The 15G is applied at a rate of 4.6 to 9.2 fl oz/1000' and the 4E at a rate of 1.6 to 2.75 fl oz/1000'.

There are label restrictions that each formulation can be used only one time per season. The 4E formulation should not be applied within 30 days of harvest and not more than 2.8 lbs. a.i./A are to be applied.

Nature of Residue

No data were submitted with this petition. Plant metabolism data are available on beans and corn and animal metabolism data are available on rats and chickens. These data were reviewed with PP#'s, 3F1306 (see memo of 3/1/73, F. Gee) and 4F1445 (see memo 5/3/74, A. Smith).

The results of these studies show that chlorpyrifos and its metabolite 3,5,6-trichloropyridinol (TCP) are absorbed and translocated in plants. The significant product of

chlorpyrifos metabolism is TCP which could be metabolized via dechlorination of the ring, formation of diols and triols and subsequently cleavage of the pyridine ring.

The nature of the residues of chlorpyrifos is adequately understood. The significant residues in both plants and animals are the parent compound and its metabolite, TCP.

Analytical Method

The sample was extracted with a mixture of 25% acetone in methylene chloride. The TCP fraction was extracted into a 1% sodium carbonate solution. The methylene chloride containing chlorpyrifos was dried through sodium sulfate and evaporated to a small volume for chromatography. The sample was then chromatographed through activated charcoal (DARCO G60) with methylene chloride used as the eluting solvent. This solution contained the chlorpyrifos fraction.

The sodium carbonate solution was then acidified with sulfuric acid and the TCP extracted with methylene chloride. This solution was dried over anhydrous sodium sulfate, evaporated to dryness and the residue was taken up in benzene. The resulting solution was then treated with N,0-bis (trimethylsilyl) acetamide (BSA) to form the pyridinol trimethylsilyl derivative. This contains the TCP fraction.

Both chlorpyrifos and TCP are determined by gas chromatography using the electron capture detector. Recoveries ranged from 70 to 114% averaging 93%.

Adequate analytical methodogy is available for enforcement purposes.

Residue Data

The residue data submitted consists of a study conducted on kale in the State of Washington in 1981. Lorsban 4E formulation was applied at the time of planting of seeds as a water based spray for shallow incorporation into the soil. Another application was made 28 days later as a directed spray at the base of the plant. The indicated application rates were 1.6 fl. oz/1000' row and twice this dosage.

The petitioner refers to this as 1X and 2X application. However, the recommended rate is 1.6 to 2.75 fl. oz./1000' row. Using the maximum rate of 2.75 the 1.6 and 3.2 fl. oz/1000' row rates represent 0.6X and 1.2X. The label restricts the applications to one per season. By making two applications the rates would, in a sense, be equivalent to 1.2X (1X) and 2.4X (2X). (This is actually not correct though because the major portion of the residue would result from

base of plant application and only one of the applications was to the base. Hence the 1X and 2X would not apply in case of transplants.)

Samples for analysis were taken 30 days after the last application. Residues ranged up to 0.007 and 0.005 ppm for chlorpyrifos for the 1X and 2X applications respectively. Residues of pyridinol ranged up to 0.007 and 0.008 ppm for the 1X and 2X applications respectively.

The data submitted are inadequate to make a conclusion as to the appropriateness of the tolerance proposed for kale. (This same conclusion applies to the other leafy crops, collards, rape and mustard.) More studies would be needed to reflect usage of the pesticide in other growing regions. The studies should reflect the usage as proposed on the label, i.e., one application either incorporated into the soil at planting for seeds or applied to the base of the crop for transplants. We recognize that there are some supporting data available for turnip greens but some data should be submitted for leafy crops in this grouping, i.e., mustard, kale, collards, rape.

Based on data reviewed with an earliar petition on broccoli, brussels sprouts, cabbage, Chinese cabbage and cauliflower, we would consider the data adequate to reflect expected residues in Chinese broccoli, broccoli raab, kohlrabi and Savoy cabbage.

There is no official grouping of brassica leafy vegetables for purposes of tolerance setting. (This grouping has been proposed, 47 FR 20635-9, but a final order has not been issued). Thus, a tolerance for this crop grouping could not be issued at this time. The only crop grouping for leafy vegetables is in 40 CFR 180.34(f) for negligible residues; this proposal is not negligible.

We have considered establishment of tolerances for the remaining commodities in the stated crop group on an individual basis as discussed above. These additional tolerances, if and when established, should be in terms of Chinese broccoli, broccoli raab, Savoy cabbage, collards, kale, kohlrabi, mustard greens and rape greens.

At the time the new grouping is implemented, the crop grouping tolerance for brassica leafy vegetables could be established on the initiative of the Agency after the necessary data are submitted.

Meat, Milk, Poultry and Eggs

The crops involved in this proposed use may occasionally be used as feed items for livestock. The tolerances already

established for residues in meat, milk, poultry and eggs are adequate to cover any secondary residue that may occur from the proposed use.

Other Considerations

The Codex tolerance involved is for residues of the parent compound in or on kale which is at one half the proposed U.S. tolerance. There is also a Codex tolerance for Chinese cabbage of 1 ppm. The established U.S. tolerance is 2 ppm for Chinese cabbage. (See "International Residue Limit Status" sheet attached).

It does not appear that the U.S. tolerance is compatible with Codex. Furthermore, PP# 3F2884/FAP# 3H5396 has recently been submitted with the intent of revising many of the U.S. tolerances.

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Chlorpyrifos

PETITION NO. 3E2819

CCPR NO. 17

Reviewer: Jesse E. Mayes

Codex Status

Proposed U.S. Tolerances

/____/ No Codex Proposal Step 6 or above

Residue (if Step 9): parent only 1/

Residue: Chlorpyrifos & 3,5,6-trichloro-2-pyridinol

Crop(s)	Limit (mg/kg)
Chinese cabbage	1
Kale	1

Crop(s)	Tol. (ppm)
Chinese Broccoli	2 ppm
Broccoli raab	2 ppm
Savoy cabbage	2 ppm
Collards	2 ppm
Kale	2 ppm
Kohlrabi	2 ppm
Mustard greens	2 ppm
Rape greens	2 ppm

CANADIAN LIMIT

Residue:

Presumably parent on these commodities 2/

Crop	Limit (ppm)
Broccoli	0.1 2/
Cabbage	0.1 1/

MEXICAN TOLERANCIA

Residue:

Crop	Tolerancia (ppm
None (on these commodities)	

NOTES:

1/ Aside from numerical considerations, consideration needs to be given as to whether the U.S. definition can be made compatible with Codex.

2/ Negligible residue type tolerances.

cc: R.F.
Circu
Reviewer
TOX
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Petition No. 3E2819
FDA
Robert Thompson

RDI:Section Head:RSQ:Date-5/23/83:RDS:Date-5/25/83:DCR-11246
TS-769:Reviewer-JesseMayes:efs:Rm-810:CM#2:6/1/83:RCB-24