4-24-84

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

APR 24 1984

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#4F3062. Chlorpyrifos on Stone Fruit. Evaluation of analytical methods and residue data. (Accession No. 072408)

FROM: Linda L. Kutney, Chemist
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THRU: Charles L. Trichilo, Chief
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and

Toxicology Branch
Hazard Evaluation Division (TS-769)

Dow Chemical Company proposes a tolerance for combined residues of chlorpyrifos (0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate) insecticide and its metabolite 3,5,6-Trichloro-2-Pyridinol (TCP) of 3 ppm (of which no more than 2 ppm is chlorpyrifos) in or on stone fruits.

Tolerances exist for chlorpyrifos and its hydrolysis product/metabolite, TCP, for a variety of agricultural commodities (see 40 CFR 180.342) and range from 0.05 ppm to 15 ppm.

Tolerances for chlorpyrifos on stone fruit exist for cherries at 2.0 ppm and for nectarines, peaches and plums (fresh prunes) at 0.05 ppm.

Conclusions

1. The metabolism in plants and animals is adequately understood. The residues of concern are that of chlorpyrifos and its metabolite, TCP.

2. Adequate analytical methods are available for the enforcement of the proposed tolerances.

3a. Residues from the proposed use are not likely to exceed the requested tolerance of 3 ppm (of which not more than 2 ppm is chlorpyrifos) in or on stone fruits.

3b. We can draw no conclusion as to the residue level expected in dried prunes. An additional residue study is needed for dried prunes. The fresh prunes used for drying should bear residues at or near the proposed tolerance level.

4. The proposed label expresses the rate of application as lb product/Acre in 25-400 gallons of water. The dosage rate for stone fruits should be given on the label both in terms of "lbs. a.i. per 100 gal. in a dilute spray to run-off," and for concentrated sprays in terms of "apply an equivalent amount of active ingredient/A" to account for variation in tree size. A revised Section B is needed.

5. There are no feed items associated with stone fruits, and the proposed label precludes the grazing of livestock in treated areas. The petitioner should also include a label restriction precluding the feeding of cover crops. Providing the petitioner imposes this restriction, there will be no problem with secondary residues in meat, milk, poultry and eggs resulting from the proposed use. A revised Section B is needed.

6. An International Residue Limit Status sheet is attached. Because no Codex or Canadian chlorpyrifos tolerances on stone fruits are established, there is no compatability problem. There is, however, a negiligible Mexican tolerance of 0.05 ppm on peaches. The U.S. residue data show a need for the much higher tolerance proposed on stone fruits.

Codex and U.S. tolerance expressions for chlorpyrifos are not compatable in that the U.S. tolerance is in terms of chlorpyrifos and TCP. The U.S. tolerance includes TCP because this metabolite is the major part of the residue on many crops.

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Recommendation

We recommend that the proposed tolerance on stone fruits of 3 ppm combined residue of chlorpyrifos and TCP (of which no more than 2 ppm is chlorpyrifos) not be established. For a favorable recommendation, the petitioner should submit: 1)An additional residue study for dried prunes. The fresh prunes used for drying should bear residue at or near the proposed tolerance level and 2) A revised Section B (see conclusions 4 and 5 discussed above) will also be necessary.

## DETAILED CONSIDERATIONS

Manufacture and Formulation

The formulation for use on stone fruits is Lorsban® 50 W (EPA Reg. #464-552); which contains 50% technical chlorpyrifos and 50% inerts in a wettable powder. All inerts in the formulation are cleared under Section 180.1001.

The manufacturing process and the principle impurities are discussed by F. Boyd, PP#4F2999, 3/14/84. The technical product is a minimum of 94% pure. We do not foresee any residue problems in the subject crops with respect to impurities in the formulation.

Proposed Use

To control various insects infesting stone fruit crops, apply as a full-coverage foliar spray using ground application equipment when pests appear or in accordance with local conditions. Use 1 1/2 lb ai/A of concentrate or use 1 1/2 lb a.i./A in 25-400 gallons of water as a dilute spray. Do not exceed 8 applications per season. Do not allow livestock to graze in treated orchards. There is a 14 day Pre-Harvest Interval.

Nature of the Residue

No new metabolism studies were submitted in conjunction with this petition. Chlorpyrifos residue metabolism has been studied in previous submissions PP#4F1445 (beans and corn), PP#3F1306 (rats, cows, pigs and chicken). It has also been studied on another tree fruit, apples. In that study it was shown that chlorpyrifos does not readily translocate, but degrades in presence of ultraviolet light. The only metabolite formed in significant quantities which is of toxicological significance is TCP (see PP#1F2620 on apples, K. Arne, 3/24/82), the hydrolized metabolite product. TCP may then be conjugated with plant substrates.

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Animal metabolism studies have shown that chlorpyrifos is oxidized and hydrolyzed to a phosphoric acid derivative which is excreted by the animals. The TCP metabolite may be excreted or further metabolized by the animal. The residues of concern are chlorpyrifos and its pyridinol metabolite, TCP.

We conclude that the nature of the residue is adequately understood in both plants and animals, for the purposes of this petition.

Analytical Methods

Enforcement methods for chlorpyrifos and TCP residues are included in Volume II of the Pesticide Analytical Manual, (PAM). Seven enforcement methods are listed in the PAM; Method II for peaches is the most applicable to stone fruits and will be discussed here. Meat and milk methods are also included in the PAM, for chlorpyrifos.

Briefly described here, in Method II, chlorpyrifos is extracted from the fruit by blending with acetone, filtering, extracting the filtrate with methylene chloride, drying the extract with sodium sulfate and evaporating to dryness. The residue is then extracted in hexane, the insecticide is partitioned into acetonitrile, and evaporated to dryness once again. The residue is dissolved into acetone and quantitation is done using GLC with a phosphorus-specific flame photometric detector. Recoveries were reported to range from 80-94% and blanks were <0.002 ppm. Sensitivity of this method is 0.01 ppm for chlorpyrifos.

PAM Method VII is given for the TCP metabolite. Briefly, the sample is heated with methanolic sodium hydroxide, extracted and hydrolyzed to TCP and quantitated using GLC with an electron capture detector. Because the result represents total pyridinol, i.e., chlorpyrifos and TCP, chlorpyrifos must be separately quantitated and the TCP is then determined by difference. This method has a sensitivity of 0.05 ppm chlorpyrifos and TCP.

Three confirmatory methods are available for chlorpyrifos as listed in the PAM, p-values, hydrolysis and mass spectroscopy.

The residue data submitted with this petition, ACR 84.4, "Determination of Chlorpyrifos and 3,5,6-Trichloro-2-Pyridinol in Stone Fruit by Gas Chromatography" is similar to the PAM Method II. Sensitivity levels were reported to be 0.01 ppm for chlorpyrifos and 0.05 ppm for TCP.

Briefly, ACR 84.4 includes acetone extraction, acetone evaporation, dissolution of residue in water and clean-up using a $C_{18}$ Sep-Pak cartridge, methanol elution, dilution of column effluent with water, partitioning into hexane and finally, quantitation of

The TCP determination as reported in ACR 84.4 is briefly summarized here. The fruit is heated and extracted in methanolic sodium hydroxide, the alcohol evaporated out of an aliquot, the water acidified and cleaned-up using the $C_{18}$ Sep-Pak cartridge, eluted with methanol into benzene and partitioned with sodium bicarbonate. The bicarbanate is then acidified and partitioned back into benzene. An aliquot is treated with N,0-bis (trimethylsilyl) acetamide to form the pyridinol trimethyl silyl derivative which is quatitated using GLC with electron capture detection. Because this determination quantifies TCP as well as hydrolyzed chlorpyrifos, a separate determination for chlorpyrifos is necessary before TCP concentration can be calculated.

Tests were conducted on the following stone fruits: peaches, nectarines, apricots, plums, prunes, sweet cherries and sour cherries. Chlorpyrifos controls ranged from 0.000-0.066 ppm and most controls were <0.010 ppm. Recoveries of samples fortified with chlorpyrifos over a concentration range of 0.01-2.0 ppm averaged 91%, but recoveries ranged from 67-114%.

TCP controls ranged from 0.002-0.086 ppm and most were <0.030 ppm. Recoveries of samples fortified with TCP over a concentration range of 0.05-1.5 ppm averaged 85%, but recoveries ranged from 46-114%.

We conclude that adequate methodology is available to enforce the proposed tolerances.

Residue Data

Residue data were submitted for the representative commodities of the stone fruit crop grouping, sweet cherries, sour cherries, peaches and plums (fresh prunes) as well as for nectarines, apricots and prunes. Chlorpyrifos was applied at a rate of 1.5 lb a.i./A, five to nine times during the growing season. One to eight trials were conducted at each of the PHI's considered for each fruit, nine PHI ranges were used in the study, ranging from 14-31 days. Studies were conducted in California, Idaho, Michigan, New York, Oregon, Pennnsylvania, South Carolina and Washington. This is considered to be an adequate geographic representation.

Data for the combined residues of chlorpyrifos and its metabolite TCP on the stone fruit ranged from non-detectable to 2.7 ppm, at PHI's of 14-31 days. Data for chlorpyrifos residues on the stone fruit ranged from non-detectable to 1.8 ppm at PHI's of 14-31 days. Residues for the concentrated spray were slightly greater than, but approximately equivalent to, the diluted spray.

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We conclude that residues from the proposed use are not likely to exceed the residue tolerance of 3 ppm for chlorpyrifos and TCP, in or on stone fruits. We also conclude that residues of chlorpyrifos will not exceed 2 ppm in or on stone fruits resulting from the proposed use.

Very limited data are available for dried prunes. The dried prune data appear to have been obtained from fresh prunes bearing residues at about the 0.1 ppm level. No data has been submitted for dried prunes made from fresh prunes with residues at or around the proposed tolerance levels. Additional data is needed before we can draw a conclusion about whether or not pesticide residues concentrate in the dried prunes before we can determine if a food additive tolerance is necessary. Insufficient data was submitted at too low a residue level for us to conclude whether residues concentrate in dried prunes.

The proposed label expresses the rate of application as lb product/Acre in 25-400 galllons of water. The dosage rate for stone fruits should be given on the label both in terms "lbs a.i. per 100 gal. in a dilute spray to run-off," and for concentrate sprays in terms of "apply an equivalent amount of active ingredient/A" to account for variation in tree size. We recommend that a revised Section B be submitted including this additional label information.

Residues in Meat, Milk, Poultry or Eggs

There are no feed items associated with stone fruits, and the proposed label precludes the grazing of livestock in treated areas. The petitioner should, however, also include a label restriction precluding the feeding of cover crops. Providing the petitioner imposes this restriction in a revised Section B, there will be no problem with secondary residues in meat, milk, poultry and eggs resulting from the proposed use.

Other Considerations

An International Residue Limit (IRL) status sheet is attached. The IRL indicates that there are no established tolerances for chlorpyrifos in Canada or by Codex (proposed at step 9) for stone fruit.

A Mexican tolerance exists for peaches at 0.05 ppm, presumably for the chlorpyrifos parent only.

U.S. residue data for chlorpyrifos and its pyridinol metabolites indicate that the higher tolerance level of 3 ppm total residue of which no more than 2 ppm is chlorpyrifos is necessary for stone fruits grown in the U.S. No resolution is possible to conform U.S. tolerances for chlorpyrifos with Mexican tolerances and still provide an appropriate U.S. tolerance level.

The U.S. and Codex have different tolerance expressions for chlorpyrifos. The pyridinol metabolite also needs to be included in the U.S. tolerance expression because it is a major component of chlorpyrifos residues found on other raw agricultural commodities.

TS-769:RCB:L.Kutney:vg:CM#2:Rm810:X77484:4/19/8/84
cc: R.F., Circu., Reviewer, TOX, EEB, EAB, PP#4F3062
RDI: R. Quick, 4/18/84; R. Schmitt, 4/18/84

# INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Chlorpyrifos

PETITION NO 4F3062

CCPR NO. 17

Linda L Kutney 4-5-84

J. Ives 4/6/84

Codex Status

[ / ] No Codex Proposal Step 6 or above

Proposed U. S. Tolerances

Residue (if Step 9): chloropyrifos only 1/

| Crop(s) | Limit (mg/kg) |
|---|---|
| none (on stone fruit) | |

Residue: Chlorpyrifos + its Metabolit 3,5,6-Trichlom-2-Pyridinol (TCP)

| Crop(s) | Tol. (ppm) |
|---|---|
| Stone Fruit | 3 PPM Combined Resid of which no more the 2 PPM is Chlorpyrif |

CANADIAN LIMIT

Residue: _____

| Crop | Limit (ppm) |
|---|---|
| none (on stone fruit) | |

MEXICAN TOLERANCIA

Residue: _____

| Crop | Tolerancia (ppm) |
|---|---|
| peaches | 0,05* |

Notes: * Negligible residue type tolerance
1/ on other commodities

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