

US EPA ARCHIVE DOCUMENT



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

APR 30 1987

OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#7E3466. Chlorpyrifos (Lorsban®) in or on Blueberries. Evaluation of Analytical Method and Residue Data (Acc. #265508, RCB #1562).

FROM: W. T. Chin, Chemist  
Tolerance Petition Section III  
Residue Chemistry Branch  
Hazard Evaluation Division (TS-769)

*W. T. Chin*

THRU: Philip V. Errico, Section Head  
Tolerance Petition Section III  
Residue Chemistry Branch  
Hazard Evaluation Division (TS-769)

*Philip V. Errico*

TO: Jay S. Ellenberger PM #12  
Registration Division (TS-767)

and

Toxicology Branch  
Hazard Evaluation Division (TS-769)

The petitioner, IR-4, on behalf of its National Director Dr. R. H. Kupelian, and the Agricultural Experiment Station of New Jersey, is requesting the establishment of a tolerance for the combined residues of the insecticide chlorpyrifos, 0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate, and its metabolite 3,5,6-trichloro-2-pyridinol (TCP) in or on the raw agricultural commodity blueberries at 2 ppm (of which no more than 1 ppm is chlorpyrifos).

Tolerances have been established under 40 CFR 180.342 for the combined residues of chlorpyrifos and TCP in or on a variety of raw agricultural commodities at levels ranging from 0.05 to 15 ppm including pears (0.05 ppm); cranberries (1.0 ppm); apples (1.5 ppm); milk fat (0.5 ppm reflecting 0.02 ppm in whole milk); eggs (0.1 ppm); the meat, fat and meat by-products of cattle (2.0 ppm); the meat, fat and meat by-products of goats, horses, and sheep (1.0 ppm); and the meat, fat and meat by-products of hogs and poultry including turkey (0.5 ppm). A number of feed additive tolerances ranging from 0.5 to 15 ppm for chlorpyrifos and TCP have been established under 21 CFR 561.98; and a number of food additive tolerances ranging from 1.5 to 25 ppm for chlorpyrifos and TCP in oils have been established under 21 CFR 193.85.

A letter of authorization dated 9/11/86 has been sent by Robert F. Bischoff of Dow Chemical Company to Hoyt Jamerson of EPA authorizing the use of all relevant Dow data concerning chlorpyrifos in support of the IR-4 petition on blueberries.

The Chlorpyrifos Registration Standard was completed on 1/25/84.

#### CONCLUSIONS

1. The nature of chlorpyrifos residues in blueberries is adequately defined for the purpose of this IR-4 petition. The residues of concern in or on blueberries are chlorpyrifos, per se, and its metabolite TCP.
2. The nature of residues in animals is not adequately understood. Additional animal metabolism studies in ruminants and poultry are requested in connection with the Chlorpyrifos Registration Standard (1/25/84). However, for the purpose of the proposed tolerance on blueberries and because no feed items are involved, RCB is not raising questions as to the need for animal metabolism studies.
3. Analytical methods, adequate for enforcement purposes, are available for the determination of chlorpyrifos, per se, and its metabolite, TCP, in plant (including blueberries) and animal commodities. Additional methodologies, however, may be needed for any future plant and animal metabolites of toxicological significance.
- 4a. The petitioner is requested to revise Section B indicating the minimum interval in days between applications. The available data support a minimum of 14-day intervals between applications.
- 4b. The available field data indicate that at the proposed rate of 1.5 a.i./A, 100 to 200 gallons total volume/A/application, or to the point of drip-off were applied. The petitioner is requested to specify the rate in the revised Section B in terms of lb a.i./100 gallons sprayed to run-off.
5. Provided that the petitioner revise Section B as stated in Conclusion 4a, RCB can conclude that the maximum combined residues of chlorpyrifos and TCP did not exceed the proposed tolerance of 2.0 ppm.
6. No feed items are involved in the proposed use of chlorpyrifos on blueberries. Therefore, RCB does not expect any secondary residues in meat, milk, poultry and eggs from the proposed use.
7. An International Residue Limits Status sheet is attached. There are no Codex, Canadian, or Mexican tolerances for chlorpyrifos on blueberries. Therefore, no compatibility questions exist with respect to Codex.

2

## RECOMMENDATION

At this time, RCB recommends against the proposed tolerance because of the deficiencies identified in Conclusion 4a and 4b.

## DETAILED CONSIDERATIONS

### Manufacture Processes

The manufacturing processes of chlorpyrifos are described in Appendix A of the Chlorpyrifos Registration Standard dated 1/25/84 and in a follow-up review (see G. P. Makhijani's 7/30/85 memo). The technical product is a minimum of 94% pure. RCB does not foresee any residue problems in the subject crop with respect to impurities in the formulation.

### Formulation

The formulation recommended for use on blueberries is Lorsban® 50W (EPA Reg. No. 464-552) which is a wettable powder containing 50% technical chlorpyrifos and 50% inerts. All inerts in the formulation have been cleared for use under 40 CFR 180.1001 (see PP#4F3062).

### Proposed Use

For control of various insects infesting blueberries, Lorsban® 50W is to be applied foliarly using ground equipment. Application may begin when pests appear or in accordance with local conditions. The proposed rate is 1.5 lb a.i./A/application for a maximum of three applications per season. There is a 28-day PHI. The proposed label warns against tank mixing with pesticides, surfactants, or fertilizer formulations unless prior use has shown the combination noninjurious under local conditions of use. All other labeling precautions and directions on the registered Lorsban® 50W label are to be observed.

The petitioner is requested to revise Section B indicating a minimum interval in days between applications. The available data support a minimum of 14-day intervals between applications.

The available field data indicate that at the proposed rate of 1.5 lb a.i./A, 100 to 200 gallons total volume/A/application, or to the point of drip-off were applied. The petitioner is requested to specify the rate in the revised Section B in terms of lb a.i./100 gallons sprayed to run-off.

## Nature of the Residue

### Plant Metabolism Study

No new plant metabolism studies were submitted with this petition. Chlorpyrifos plant metabolism studies have been reviewed in previous submissions PP# 4F1445 (beans and corn) and PP#OF2350 (apple, pears, cherries, peaches, red currants, sugar beet leaves, savoy cabbage and spinach). In those studies, it was found that chlorpyrifos does not readily translocate, but degrades in the presence of UV light. TCP, a hydrolyzed product of the parent, is the only metabolite formed in significant quantities and is of toxicological significance. TCP may then be conjugated with plant substrates (see PP#1F2620 on apple, K. Arne, 3/24/82).

The conclusions of the chlorpyrifos plant metabolism studies mentioned above may be extended to include blueberries. The residue of concern for this use on blueberries is chlorpyrifos, per se, and its metabolite 3,5,6-trichloro-2-pyridinol (TCP).

### Animal Metabolism Study

No new animal metabolism studies were submitted with this petition. Previous chlorpyrifos animal metabolism studies have shown that chlorpyrifos is oxidized and hydrolyzed to a phosphoric acid derivative which is excreted by animals. The TCP metabolite may be excreted or further metabolized by animals. RCB has previously concluded that the residues of concern consist of the parent, chlorpyrifos, per se, and its TCP metabolite (see PP#'s 3F1306, 9F2270, OF2281 and PP#6F3358, 9/30/86).

The nature of residues in animals is not adequately understood. Additional animal metabolism studies in ruminants and poultry are requested in connection with the Chlorpyrifos Registration Standard (1/25/84). However, for the purpose of the proposed tolerance on blueberries and because no feed items are involved, RCB is not raising questions as to the need for animal metabolism studies.

### Analytical Methods

Seven enforcement methods for the determination of chlorpyrifos and TCP residues in different commodities are included in PAM II. In this petition, a method (Dow's ACR 84.4) entitled "Determination of Chlorpyrifos and TCP in Stone Fruit by Gas Chromatography" was used to determine chlorpyrifos residue in blueberry samples. This method is the same as that discussed in connection with PP#4F3062

4

for residue analysis in stone fruits. It is also similar to Method II in PAM II. The method is applicable to peaches, plums, nectarines, apricots, prunes, sweet and sour cherries.

Briefly, chlorpyrifos is extracted from the stone fruit by blending with acetone. The acetone extract is evaporated and the chlorpyrifos residue is taken up in water for cleanup by passing through a C<sub>18</sub> Sep-Pak column. Chlorpyrifos is eluted from the column with methanol and the effluent is diluted with water. Chlorpyrifos is extracted from the water with a known volume of hexane and then determined by gas chromatography equipped with a flame photometric detector. The sensitivity of this method is 0.01 ppm for chlorpyrifos. Recoveries of blueberry samples fortified with chlorpyrifos over a concentration range of 0.01 to 2.00 ppm ranged from 68% to 104%, averaging 90±8%.

PAM Method VII was used for the determination of TCP residue in blueberry samples. This method is included in method ACR 84.4 which was also discussed in PP#4F3062. Briefly, samples are heated with methanolic sodium hydroxide before extraction. Any chlorpyrifos present is hydrolyzed and determined by gas chromatography with an electron capture detector. Since the analysis is for total pyridinol (including chlorpyrifos), duplicate samples must be analyzed for chlorpyrifos by this method. The TCP residue is calculated by difference. The sensitivity of this method for TCP is 0.05 ppm. Recoveries of blueberry samples fortified with TCP over a concentration range of 0.5 to 4.0 ppm ranged from 60% to 102%, averaged 85±10%.

Adequate validation data and examples of gas chromatograms and calculations were submitted. Analytical methods, adequate for enforcement purposes, are available for the determination of chlorpyrifos, per se, and its metabolite, TCP, in plant (including blueberries) and animal commodities. Additional methodologies, however, may be needed for any future plant and animal metabolites of toxicological significance.

#### Storage Stability Study

Storage stability studies for chlorpyrifos and TCP residues in or on several plant and animal commodities have been 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 -18°C to -20°C.

#### Residue Data

Seven field experiments were conducted between 1983 and 1985 in six states (New Jersey, Michigan, Oregon, New York, Pennsylvania and Washington). This represents

the major blueberry growing area in the United States. Lorsban® 50W insecticide was applied three times during the growing season at the rate of 3 lb (1.5 lb a.i.) per acre per application as a foliar spray. The applications were made at approximately 14-day intervals. Blueberries were sampled from 1 to 29 days after last application. Samples were hand picked at random from at least 12 bushes or plants, then stored frozen at -18°C until analyzed. The residue data of the seven field trials are summarized in Table 1 (see PP#7E3466, Acc. #265508, p.12).

Table 1. The Combined Residues of Chlorpyrifos and TCP in/on Blueberries from Three Applications at 1.5 lb a.i./A/Application

Location	PHI (day)	Maximaum Residue Found (ppm)		
		Chlorpyrifos*	TCP**	Total
Fennville, MI	15	0.18	0.17	0.35
	29	0.02	0.09	0.11
Grand Junction, MI	14	0.09	0.23	0.32
	28	0.04	0.22	0.26
Chatsworth, NJ	1	1.8	0.72	2.52
	3	1.9	0.47	2.37
	7	0.27	0.41	0.68
	14	1.1	<0.05	1.15
	21	0.02	<0.05	0.07
Geneva, NY	14	0.02	0.12	0.14
	28	0.02	0.13	0.15
Aurora, OR	15	1.9	1.3	3.2
	29	0.56	0.45	1.01
Upper Black Eddy, PA	14	0.40	0.25	0.65
	21	0.08	0.27	0.35
	28	0.12	0.26	0.38
Vancouver, WA	14	0.96	0.68	1.64
	28	0.37	0.23	0.60

\* Corrected for average recovery of 90%.

\*\* Corrected for control, average recovery of 85% and the TCP contributed by alkaline hydrolysis of chlorpyrifos.

6  
420

The residue data shown in Table 1 indicate that the maximum combined residues of chlorpyrifos and TCP, at 14-day interval between applications and a PHI of 28 days, did not exceed 2.0 ppm. Therefore, with a revised Section B as stated under the Proposed Use, RCB can conclude that the residue data are adequate to support the proposed tolerance.

#### Residues in Meat, Milk, Poultry and Eggs

There are no feed items involved with this use on blueberries. Therefore, RCB does not expect problems with secondary residues in meat, milk, poultry and eggs resulting from the proposed use. Existing tolerances for livestock commodities will not be affected by the proposed use on blueberries.

#### Other Considerations

An International Residue Limits Status sheet is attached. There are no Codex Canadian, or Mexican tolerances for chlorpyrifos on blueberries. Therefore, no compatibility questions exist with respect to Codex.

Attachment: IRLS sheet.

cc: Ciri., R.F., W.T.Chin, PP#7E3466, TOX, RD, PM#12, EAB, EEB and PMSD/ISB  
RDI: P.V.Errico(4/23/87): R.D.Schmitt(4/24/87)  
TS-769: RCB: CM#2: RMB12:557-4352: W.T.Chin,wc(4/27/87)



INTERNATIONAL RESIDUE LIMIT STATUS

*J. Alves*  
*1/9/87*

CHEMICAL Chlorpyrifos

PETITION NO. 7E3466

CCPR NO. 17

Reviewer: W. T. Chin

Codex Status

Proposed U.S. Tolerances

No Codex Proposal  
Step 6 or above on  
blueberries

Residue (if Step 9): \_\_\_\_\_

Residue: Chlorpyrifos and its  
metabolite, 3,5,6-Trichloro-2-pyridinol (TCP)

Crop(s)    Limit (mg/kg)

Crop(s)    Tol. (ppm)

Blueberries    2 ppm

CANADIAN LIMIT

MEXICAN TOLERANCIA

Residue: \_\_\_\_\_

Residue: \_\_\_\_\_

Crop    Limit (ppm)

Crop    Tolerancia (ppm)

none (on blueberry)

none (on blueberry)

NOTES:

*8*  
*460*