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

OCT 18 1985

OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#5F3286 [RCB Nos. 1306, 1307, and 1308].  
Chlorpyrifos on Fruiting Vegetables  
(Except Cucurbits) - Crop Group VIII  
Commodities. Evaluation of Analytical  
Methods and Residue Data (Accession No. 073734).

FROM: Michael P. Firestone, Ph.D., Chemist  
Tolerance Petition Section II  
Residue Chemistry Branch  
Hazard Evaluation Division (TS-769)

THRU: Charles L. Trichilo, Chief  
Residue Chemistry Branch  
Hazard Evaluation Division (TS-769)

TO: Jay S. Ellenberger, Product Manager (12)  
Insecticide-Rodenticide Branch  
Registration Division (TS-767)

and

Toxicology Branch  
Hazard Evaluation Division (TS-769)

Dow Chemical Company is proposing the establishment of a tolerance for combined residues of the insecticide chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate] and its metabolite 3,5,6-trichloro-2-pyridinol (TCP) in or on crop group VIII commodities - fruiting vegetables (except cucurbits) at 1.5 ppm (of which no more than 1.0 ppm is chlorpyrifos). The representative group VIII crops are tomatoes and peppers.

Tolerances for combined residues of chlorpyrifos plus TCP in/on a wide variety of agricultural commodities have been established under 40 CFR 180.342 at levels ranging from 0.05 to 15 parts per million. In conjunction with PP#3F2884/FAP#3H5396, RCB has recommended for proposed revisions of several established tolerances in which the amount of chlorpyrifos, per se, would be specified but the combined residue level of parent plus TCP would not change (see K. Arne memorandum of January 24, 1984).

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Tolerances have been established for chlorpyrifos plus TCP residues in/on imported tomatoes at 0.5 ppm and imported peppers at 1.0 ppm (see PP#8E2092 and PP#1E2523, respectively). In the subject petition, additional residue data on tomatoes and peppers grown within the United States have been submitted.

In conjunction with PP#4F3008/FAP#1H5295, RCB has recommended previously for establishment of tolerances for combined residues of chlorpyrifos plus TCP in/on tomatoes at 1.5 ppm (of which no more than 1.0 ppm is chlorpyrifos), tomato pomace at 100 ppm (of which no more than 65 ppm is chlorpyrifos), and various animal commodities (see R. Cook memorandum of March 6, 1984).

A Registration Standard for chlorpyrifos was completed on September 30, 1984.

Conclusions:

- 1a. The use pattern proposed in the subject petition for fruiting vegetables (including tomatoes) is identical to that proposed in conjunction with FAP#1H5295 for chlorpyrifos application to tomatoes (see K. Arne memorandum of November 21, 1983). RCB has previously recommended in favor of the proposed use on tomatoes (see R. Cook memorandum of March 6, 1984, re: PP#4F3008/FAP#1H5295).
- 1b. Tolerances have already been established for chlorpyrifos plus its metabolite 3,5,6-trichloro-2-pyridinol (TCP) in/on imported tomatoes at 0.5 ppm and imported peppers at 1.0 ppm (see PP#8E2092 and PP#1E2523, respectively).
- 2a. Since this petition is intended to establish a crop group VIII tolerance for which tolerances are already established on the representative commodities tomatoes and peppers, the nature of the residue in/on fruiting vegetable crops (except cucurbits) is considered adequately understood for the purpose of this petition only. The residues of concern are chlorpyrifos and its metabolite TCP.
- 2b. Since the only animal feed item involved in this petition is tomato pomace, for which RCB has previously recommended for establishing a tolerance in terms of chlorpyrifos and its metabolite TCP (see R. Cook memorandum of March 6, 1984, re: PP#4F3008/FAP#1H5295), the nature of the residue in animals will be considered adequately understood for the purposes of this petition only. The residues of concern consist of chlorpyrifos and its metabolite TCP.

3. RCB concludes that adequate analytical methodology is available for the enforcement of residues of chlorpyrifos and its metabolite TCP in/on fruiting vegetables (except cucurbits).
- 4a. Based on the available residue data, RCB does not expect maximum levels of chlorpyrifos plus TCP to exceed 1.5 ppm on fresh tomatoes as a result of the proposed use. However, the levels of chlorpyrifos residues on peppers will be higher than 1.5 ppm (see Conclusion 4c below).
- 4b. As a result of the proposed use on tomatoes, the maximum expected residue level for (dry) tomato pomace is 100 ppm (of which no more than 65 ppm will consist of chlorpyrifos).

In conjunction with PP#4F3008/FAP#1H5295, RCB has already recommended for establishment of a 100 ppm tolerance (of which no more than 65 ppm consists of chlorpyrifos) covering residues in tomato pomace (see R. Cook memorandum of March 6, 1984). Since the chlorpyrifos use on tomatoes proposed in conjunction with PP#4F3008/ FAP#1H5295 is identical to that proposed in conjunction with the subject petition, there is no need for any new tolerance proposal for tomato pomace here.

- 4c. Based on the proposed use, RCB does not expect maximum chlorpyrifos plus TCP levels to exceed 3.0 ppm in/on treated peppers. This is the level at which a group tolerance for fruiting vegetables (except cucurbits) would need to be established.

The petitioner should submit a revised Section F in which the proposed tolerance for residues of chlorpyrifos plus TCP in fruiting vegetables (except cucurbits) is set at 3.0 ppm.

- 4d. The petitioner will need to withdraw the 1.5 ppm chlorpyrifos plus TCP tolerance covering residues in tomatoes proposed in conjunction with PP#4F3008 since tomatoes are included under fruiting vegetables (except cucurbits) - crop group VIII commodities.
- 4e. At such time as a crop group VIII tolerance is established for chlorpyrifos, existing tolerances covering residues in tomatoes and peppers established under 40 CFR 180.342 at 0.5 and 1.0 ppm, respectively, should be withdrawn.

5. The only animal feed item resulting from the proposed use of chlorpyrifos on fruiting vegetables (except cucurbits) is tomato pomace. The likely level of secondary residues resulting in animal commodities from the proposed use of chlorpyrifos on tomatoes has already been extensively discussed in RCB's review of FAP#1H5295 (see K. Arne memorandum of November 21, 1983). Thus, no new issues are involved in conjunction with the subject petition.

For approval of the proposed chlorpyrifos tolerance for fruiting vegetables (except cucurbits), the following animal commodity tolerances for which RCB has previously recommended in favor of in conjunction with PP#4F3008/ FAP#1H5295 (see R. Cook memorandum of March 6, 1984) will also need to be established:

Milk, fat: 0.5 ppm (of which no more than 0.25 ppm is chlorpyrifos);  
Milk, whole: 0.03 ppm (of which no more than 0.02 ppm is chlorpyrifos);  
Meat, fat, and meat byproducts of cattle:  
2.5 ppm (of which no more than 2 ppm is chlorpyrifos);  
Meat, fat, and meat byproducts of goats and sheep:  
2 ppm (of which no more than 1 ppm is chlorpyrifos);  
Meat, fat, and meat byproducts of hogs:  
0.5 ppm (of which no more than 0.3 ppm is chlorpyrifos);  
Meat, fat, and meat byproducts of horses:  
1.5 ppm (of which no more than 0.8 ppm is chlorpyrifos).

6. An International Residue Limit Status sheet is included with this review as Attachment 1. There are no Canadian or Mexican limits/tolerances covering chlorpyrifos residues in/on any fruiting vegetables (except cucurbits). Codex has established indicator compound limits (i.e., reflecting parent compound only) of 0.2 ppm for eggplants, and 0.5 ppm for peppers and tomatoes. These limits are not compatible with either the proposed U.S. tolerance expression (covering residues of parent compound plus TCP) or the actual maximum levels of chlorpyrifos only (up to 0.92 ppm in tomatoes and 1.6 ppm in peppers).

Recommendation:

At this time, RCB recommends against establishing the chlorpyrifos tolerance on crop group VIII fruiting vegetables for the reasons cited under Conclusions 4c and 4d.

The PM and the petitioner should be aware of Conclusions 4e and 5.

## Detailed Considerations

### Manufacturing and Formulation

The chlorpyrifos manufacturing process was described in Confidential Appendix A of the Registration Standard. Technical chlorpyrifos is at least 94 percent pure. Numerous data gaps involving the product chemistry were cited in the Registration Standard and remain outstanding (see Chlorpyrifos Registration Standard and Dow's response to residue chemistry data gaps, R. Loranger memorandum of March 25, 1985).

The formulation proposed for use on eggplants, peppers, and tomatoes is a 50% wettable powder formulation - Lorsban 50W Insecticide. The composition of this formulation (containing 53.2% technical chlorpyrifos) is discussed in RCB's review of PP#9F2221 (see E. Leovey memorandum of February 8, 1980). All inerts in this formulation are cleared under 40 CFR 180.1001.

Since this petition involves only expansion of currently established chlorpyrifos tolerances for tomatoes and peppers to a crop group VIII tolerance for fruiting vegetable crops except cucurbits (note: tomatoes and peppers are the only crop group VIII representative commodities), the chlorpyrifos product chemistry will be considered adequately described for the purposes of this petition only.

### Proposed Use on Fruiting Vegetable Crops (Except Cucurbits)

Lorsban 50W Insecticide is proposed for use on eggplants, peppers, (chili, sweet, bell, and pimento), and tomatoes, while Lorsban 4E Insecticide is proposed for use on tomatoes only.

Chlorpyrifos is to be applied at a rate of 1 lb ai (2 lb Lorsban 50W or 1 qt Lorsban 4E) per acre. A maximum of 10 applications may be made per season, none within 7 days before harvest (i.e., PHI = 7 days).

The above-proposed use pattern is identical to that proposed in conjunction with FAP#1H5295 for chlorpyrifos application to tomatoes (see K. Arne memorandum of November 21, 1983). This use on tomatoes has been recommended for by RCB in conjunction with PP#4F3008/ FAP#1H5295 (see R. Cook memorandum of March 6, 1984).

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## Nature of the Residue

### a. Plants

The nature of the residue in plants has been extensively discussed in RCB's review of FAP#1H5295 - Chlorpyrifos on Tomato Pomace (see K. Arne memorandum of November 20, 1981) and in the Chlorpyrifos Registration Standard (September 30, 1984).

Since this petition is intended to establish a crop group VIII tolerance for which tolerances are already established on the representative commodities tomatoes and peppers, the nature of the residue in/on fruit vegetable crops (except cucurbits) is considered adequately understood for the purpose of this petition only. The residues of concern are chlorpyrifos and its metabolite TCP.

With regard to resolving legume, corn, and root crop metabolism data gaps cited in the Chlorothalonil Registration Standard, Dow has stated its intention to conduct corn and sugarbeet metabolism studies (see N. Dodd memorandum of July 15, 1985, re: EPA Registration No. 464-523).

### b. Animals

The nature of the residue in animals has been extensively reviewed in the Chlorpyrifos Registration Standard (September 30, 1984) in which the following animal metabolism data gaps were cited:

- i. Ruminant metabolism study reflecting dermal application (dip treatment);
- ii. Poultry metabolism study reflecting 3-day oral dosing.

RCB has previously recommended for tolerances of 1.5 ppm in or on tomatoes and 100 ppm in or on tomato pomace in terms of chlorpyrifos plus its metabolite TCP (see R. Cook memorandum of March 6, 1984, re: PP#4F3008/FAP#1H5295). Since the poultry dietary intake of tomato pomace is very small, RCB concludes that the nature of the residue in animals will be considered adequately understood for the purposes of this petition only.

The residues of concern in animals consist of chlorpyrifos and its metabolite TCP.

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Analytical Methodology

The method of Miller and McKellar designated ACR 84.4 is proposed for regulatory purposes. Chlorpyrifos is determined separately, then all residues hydrolyzable to 3,5,6-trichloro-2-pyridinol or TCP (including chlorpyrifos) are determined. The amount of TCP is calculated by difference. This method is similar to that found in PAM-II, and previously used to generate residue data on treated tomatoes (see K. Arne memorandum of November 20, 1981, re: FAP#1H5295).

a. Chlorpyrifos

Chlorpyrifos residues are extracted with acetone, the acetone is evaporated, the residues are taken up in water, and cleaned up on a C<sub>18</sub> Sep-Pak column. Chlorpyrifos is extracted from water using hexane and then determined by gas-liquid chromatography using a flame photometric detector.

The following chlorpyrifos fortification-recovery data were reported.

Sample	Fortification (ppm)	Percent Recovery	
		Range	Average (n)
peppers	0.01-2.0	70-110	86 (46)
tomatoes	0.01-0.5	15-110	94 (16)

n = number of fortified samples analyzed.

The reported limit of detection for chlorpyrifos is 0.01 ppm. Control values were all < 0.01 ppm except for one sample (0.08 ppm).

3,5,6-Trichloro-2-pyridinol (TCP)

Fruiting vegetable samples are heated with 10 percent sodium hydroxide/methanol (to convert residues to TCP) and extracted by shaking. The extracts are evaporated to remove the methanol, dilute acid solution is added, and then the mixture is cleaned up on a C<sub>18</sub> Sep-Pak column. TCP is eluted with methanol, diluted with sodium bicarbonate solution, and partitioned with benzene. Following acidification and back-partitioning with benzene, the benzene phase is treated with N-O-bis(trimethylsilyl)acetamide to form a pyridinol trimethylsilyl derivative which is quantitated by gas-liquid chromatography using an electron capture detector.



The following TCP fortification-recovery data are reported:

Sample	Fortification (ppm)	Percent Recovery Range	Average (n)
peppers	0.05-5.0	70-124	91 (42)
tomatoes	0.05-2.0	76-110	92 (20)

n = number of fortified samples analyzed.

The reported limit of detection for TCP is 0.05 parts per million. Control samples ranged from < 0.05 to 0.07 parts per million.

RCB concludes that adequate analytical methodology is available for the enforcement of residues of chlorpyrifos and its metabolite TCP in/on fruiting vegetables (except cucurbits).

#### Residue Data

The storage stability of chlorpyrifos in frozen plant samples is extensively discussed in the Chlorpyrifos Registration Standard. Residues of chlorpyrifos or TCP in various fruits, vegetables, and nuts ranged from 66 to 109 percent (average = 85%) of the initial fortification levels (0.1 to 1.0 ppm) after storage at -18 °C (0 °F) for 5 to 27 months. After 4 years of frozen storage, residues in apples and walnuts ranged from 61 to 105 percent and 82 to 100 percent, respectively, of their initial fortification levels. After 29 months of frozen (-18 °C) storage in tomatoes, residues of chlorpyrifos and TCP ranged from 82 to 88 percent and 89 to 109 percent, respectively, of their initial fortification levels.

In conjunction with this petition, pepper and tomato plants were treated during 1983. Samples were harvested from June until September, placed in frozen storage the same day as collected, shipped with dry ice to Dow's Michigan laboratory, ground in a Hobart food cutter, then stored at -18 °C until analyzed. Although the dates of analyses are not stated, considering the date of the residue data report is June 1985, (i.e., length of storage =  $\leq$  2 years), RCB has no concern with regard to the degradation of residues in stored samples.

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a. Tomatoes

In conjunction with FAP#1H5295 (see K. Arne memorandum of November 21, 1983), RCB reviewed residue data generated during 1982 representing a total of 12 field trials conducted in the States of California, Florida, Georgia, Illinois, Indiana, Michigan, New York, Pennsylvania, and South Carolina. These data are summarized in the table below. (Note: the use proposed in the subject petition for fruiting vegetables including tomatoes, peppers, and eggplants and in PP#4F3008/FAP#1H5295 for tomatoes allows up to 10 applications of chlorpyrifos at 1.0 lb ai/A, with a minimum PHI of 7 days):

Number of 1.0 lb ai per acre applications	PHI (Days)	Residue Levels (ppm)		Total
		Chlorpyrifos	TCP	
9-10	0	0.09-1.7	0.06-0.32	0.09-1.96
9-10	7	0.03-0.92	< 0.05-0.37	0.09-1.16
9-10	14	0.01-0.94	< 0.05-0.15	0.08-1.02
9-10	21-24	0.02-0.40	< 0.05-0.40	< 0.08-0.76

In the subject petition, additional residue data generated on tomatoes (including cherry varieties) have been submitted representing a total of 30 field trials conducted in the States of California, Mississippi, New York, Oregon, Texas, Florida, Illinois, Michigan, and New Jersey. These additional data are summarized in the following table:

Number of 1.0 lb ai per acre applications	PHI (Days)	Residue Levels (ppm)		Total
		Chlorpyrifos	TCP	
<b>Cherry Tomatoes:</b>				
8-11	7	0.01-0.60	< 0.05-0.78	< 0.05-1.10
8-11	14	< 0.01-0.38	< 0.05-0.50	0.13-0.73
8-11	21	< 0.01-0.07	< 0.05-0.31	< 0.09-1.02
<b>Large Variety Tomatoes:</b>				
7-11	7	0.01-0.44	< 0.05-0.43	0.07-0.71
7-11	14	0.01-0.16	< 0.05-0.45	< 0.09-0.57
7-11	21	< 0.01-0.09	< 0.05-0.26	0.08-0.37

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Although all the residue data reflect ground application, RCB has previously concluded that residues from aerial application are not expected to be higher than those resulting from ground application (see K. Arne memorandum of November 21, 1983, re: FAP#1H5295).

Based on the above data, RCB does not expect maximum chlorpyrifos plus TCP levels to exceed 1.5 ppm in/on tomatoes as a result of the proposed use.

b. Processed Tomatoes

The results of a tomato processing study, discussed in RCB's review of FAP#1H5295 (see K. Arne memorandum of November 20, 1981), are summarized in the table below:

Sample	Residue Level (ppm)			Concentration Factor
	Chlorpyrifos	TCP	Total	
whole tomato	0.38	0.15	0.53	---
juice	< 0.01	0.09	0.10	0.19
puree	0.05	0.16	0.21	0.40
wet pomace	1.6	0.85	2.45	4.62
wet pomace	1.3	0.3	1.6	---
dry pomace	18.0	3.0	21.0	13.1

Total (chlorpyrifos plus TCP) residues concentrate approximately 5x going from whole tomatoes to wet pomace. Upon drying, an additional thirteen-fold concentration occurs. On this basis, a concentration factor of approximately 65 (13 x 5) is observed for dry tomato pomace.

Based on a maximum expected level of 1.5 ppm total chlorpyrifos in/on whole tomatoes as a result of the proposed use, and a concentration factor of 65, the maximum level of chlorpyrifos plus TCP is not expected to exceed 100 ppm in tomato pomace.

In conjunction with PP#4F3008/FAP#1H5295, RCB has already recommended for establishment of a 100 ppm tolerance covering residues in tomato pomace (see R. Cook memorandum of March 6, 1984). Since the chlorpyrifos use on tomatoes proposed in conjunction with PP#4F3008/FAP#1H5295 is identical to that proposed in conjunction with the subject petition, there is no need for any new tolerance proposal for tomato pomace here.

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c. Peppers

Residue data were generated on both bell and small varieties of peppers grown in the States of Mississippi, Texas, California, Florida, New Jersey, New York, Oregon, Michigan, and Illinois. The proposed use of chlorpyrifos on peppers (maximum of ten 1.0 lb ai/A applications, PHI = 7 days) is the same as that for tomatoes. Tabulated below is a summary of the pepper residue data:

Number of 1.0 lb ai per acre applications	PHI (Days)	Residues Levels (ppm)		
		Chlorpyrifos	TCP	Total
Small Peppers:				
5-10	7	0.01-1.60	< 0.05-0.89	0.09-2.50
5-10	14	0.04-1.00	< 0.05-0.13	< 0.09-1.05
5-10	21	< 0.01-0.29	< 0.05-0.23	< 0.09-0.52
Bell Peppers:				
7-10	7 or 8	0.05-0.92	< 0.05-0.20	< 0.09-1.10
7-10	14	0.03-0.52	< 0.05-0.21	< 0.08-0.73
7-10	21	< 0.01-0.42	< 0.05-0.48	< 0.06-0.56

Based on the proposed use, RCB does not expect maximum chlorpyrifos plus TCP levels to exceed 3.0 ppm in/on treated peppers.

The petitioner should submit a revised Section F in which the proposed tolerance for residues of chlorpyrifos plus TCP in fruiting vegetables (except cucurbits) is set at 3.0 parts per million.

In addition, the petitioner should withdraw the 1.5 ppm chlorpyrifos tolerance for tomatoes proposed in conjunction with PP#4F3008.

Finally, should the crop group (VIII) tolerance be established for fruiting vegetables (except curcurbits), existing tolerances established under 40 CFR 180.342 for tomatoes at 0.5 ppm and peppers at 1.0 ppm should be withdrawn.

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Residue in Meat, Fat, Milk, Poultry, and Eggs

The only animal feed item resulting from the proposed use of chlorpyrifos on fruiting vegetables (except cucurbits) is tomato pomace. The likely level of secondary residues resulting in animal commodities from the proposed use of chlorpyrifos on tomatoes has already been extensively discussed in RCB's review of FAP#1H5295 (see K. Arne memorandum of November 21, 1983). Thus, no new issues are involved in conjunction with the subject petition.

For approval of the proposed use of chlorpyrifos on fruiting vegetables (except cucurbits), the following animal commodity tolerances for which RCB has previously recommended in favor of in conjunction with PP#4F3008/FAP#1H5295 (see R. Cook memorandum of March 6, 1984) will also need to be established:

- Milk, fat: 0.5 ppm (of which no more than 0.25 ppm is chlorpyrifos);
- Milk, whole: 0.03 ppm (of which no more than 0.02 ppm is chlorpyrifos);
- Meat, fat, and meat byproducts of cattle:  
2.5 ppm (of which no more than 2 ppm is chlorpyrifos);
- Meat, fat, and meat byproducts of goats and sheep:  
2 ppm (of which no more than 1 ppm is chlorpyrifos);
- Meat, fat, and meat byproducts of hogs:  
0.5 ppm (of which no more than 0.3 ppm is chlorpyrifos);
- Meat, fat, and meat byproducts of horses:  
1.5 ppm (of which no more than 0.8 ppm is chlorpyrifos).

Other Considerations

An International Residue Limit Status sheet is attached to this review. There are no Canadian or Mexican limits/tolerances covering chlorpyrifos residues in/on any fruiting vegetables (except cucurbits). Codex has established indicator compound limits (i.e, reflecting parent compound only) of 0.2 for egg-plants, and 0.5 ppm for peppers and tomatoes. These limits are not compatible with either the proposed U.S. tolerance expression (covering residues of parent compound plus TCP) or the actual maximum levels of chlorpyrifos only (up to 0.92 ppm in tomatoes and 1.6 ppm in peppers).

Attachment 1: International Residue Limit Status Sheet

cc: R.F., Circu, M.P.Firestone, EAB, EEB, PETITION NO. 5F3286  
FDA, PMSD/ISB  
RDI:JHONLEY:10/10/85:RDSchmitt:10/10/85  
TS-769:MPFIRESTONE:CM#2:RM:800:557-7484  
typed by Kendrick: 10/15/85: edited by LDJ:10/17/85

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INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL: chlorpyrifos

PETITION NO.: 5F3286

CCPR NO.: 17

REVIEWER: Michael P. Firestone

Codex Status

No Codex Proposal Step 6 or above

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

chlorpyrifos only

Proposed U.S. Tolerances

Residue: chlorpyrifos plus  
trichloropyridinol

Crop(s)                      Limit (mg/kg)

eggplant                      1.0  
peppers                      1.5  
tomatoes                      1.5

Crop(s)                      Tol. (ppm)

Crop Group VIII Fruiting  
Vegetables including  
eggplant, peppers,  
and tomatoes                      1.5\*

\* of which no more than 1.0 ppm consists of chlorpyrifos

CANADIAN LIMIT

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

MEXICAN TOLERANCIA

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

Crop(s)                      Limit (ppm)

1.5

Crop(s)                      Tolerancia (ppm)

1.5

Notes: