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

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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

Subject: PP# 2E2584. Chlorpyrifos on grapes. Evaluation of analytical method and residue data.

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Dr. M. E. Burt and Dr. R. H. Kupelian, both of IR-4, on behalf of the IR-4 Technical Committee and the Agricultural Experiment Stations of Alabama, Arkansas, Georgia, Missouri, North Carolina, and South Carolina, propose a tolerance for the residues of chlorpyrifos (which include parent plus a metabolite 3,5,6-trichloro-2-pyridinol (TCP)) on grapes at 0.5 ppm.

Chlorpyrifos tolerances are established for several commodities ranging from 0.01 ppm for eggs to 15 ppm for peanut hulls. Many tolerances are pending. Dow Chemical Co. has submitted a letter of authorization permitting the use of chlorpyrifos data to support this petition.

Conclusions

1. The nature of the residue in plants and animals is adequately understood. The residue of conern consists of chlorpyrifos plus TCP.

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2. Adequate analytical methods are available for enforcement purposes.

3a. The proposed tolerance for grapes is adequate to cover expected residues from the proposed.

3b. No concentration of residues is expected in raisins, wet grape pomace or grape juice; no food additive tolerances are needed for these items. However, we calculate that residues may exceed 1 ppm in dried grape pomace. A feed additive tolerance of 2 ppm should be proposed for dried grape pomace.

4a. Existing or pending tolerances will accommodate any expected residues in meat, milk, poultry and eggs.

5. An International Residue Limit Statussheet is attached. The Codex MRL for chlorpyrifos on grapes is 1 ppm. However, since the definition of the residue is different (the U.S. regulates parent plus TCP, Codex regulates only parent) and since TCP can be a significant portion of the residue, the U.S. tolerance cannot be made compatible with the Codex tolerance.

Recommendation

We could, toxicological considerations permitting, recommend for the proposed tolerance on grapes provided the petitioner submits a feed additive proposal of 2 ppm for dried grape pomace. These tolerances are contingent on the establishment of the meat, milk, poultry and egg tolerances proposed with PP#0F2281.

If and when these tolerances are established their incorporation in the CFR should be accompanied by a mechanism that defines the geographic limitations of this use.

DETAILED CONSIDERATIONS

Formulation

Lorsban 4E (EPA Reg. No. 464-448) is proposed for use and contains 40.7% chlorpyrifos (4 lbs/gal). The inert ingredients, [redacted] and [redacted] are cleared for use under Sec. 180. 1001(c).

Technical chlorpyrifos has a minimum purity of 94.0%. The manufacturing process has been described in our review of PP#4F1445 (memo of 5/3/74, A. Smith). Impurities comprise [redacted] of the technical material. They are [redacted] The remainder of the non-volatiles [redacted] consist of at least seven compounds. We do not expect the impurities in Lorsban to present a residue problem due to the high dilution rates upon application.

Proposed use

For control of the grape root borer 2 qts. of a dilute spray (2.25 lb. a.i./100 gal) are to be applied to the soil surface on a 15 square foot area around the base of each vine just before the grape root borers emerge from the soil. The spray should not be allowed to contact the fruit. Only one application is allowed per season and none within 35 days of harvest.

A label restriction limits this use to states east of the Rocky Mountains (see also under Residue Data).

INERT INGREDIENT INFORMATION IS NOT INCLUDED

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Nature of the Residue

The metabolism of chlorpyrifos has been studied in corn and bean plants (PP#3F1306) and in apples and soybeans (PP# 0F2281). These studies, most recently discussed in conjunction with PP#1F2575, chlorpyrifos on citrus (see memo of 3/4/82, K. Arne), show that chlorpyrifos does not readily translocate, that it degrades in the presence of UV light and that while several metabolites may be formed the only ones formed in significant quantities is TCP. TOX has judged that unidentified metabolites uncovered in the apple and soybean studies are not of toxicological significance (see PP#0F2281, memo of 10/21/81, W. Dykstra and Section 18 for chlorpyrifos on soybeans, memo of 8/11/81, A. Mahfouz). We therefore reiterate our conclusion (made in conjunction with several petitions) that the nature of the residue in plants is adequately understood. The residue of concern consists of parent plus TCP. Residues resulting from the proposed use are probably as a result of spray drift.

A summary of animal metabolism studies is available in our review of PP#1F2575 (memo of 3/14/82, K. Arne). The metabolism of chlorpyrifos has been studied in rats and cows (PP# 3F1306, see memo of F. D. R. Gee, 3/1/73) and in goats (PP# 0F2281, see memo of 7/7/81 E. Leovey). In these studies the major metabolites uncovered were chlorpyrifos and TCP (plus conjugates of TCP). The nature of the residue in animals is adequately understood. The residue of concern consists of parent plus TCP.

Analytical Methods

The residue data in this petition were obtained by the PAM II methods described below. Chlorpyrifos and TCP are determined separately.

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Chlorpyrifos

The plant sample is extracted with acetone. An aliquot of the acetone is evaporated to near dryness. The residue is transferred to a 5% sodium sulfate solution; the chlorpyrifos is then extracted into hexane. The sample is cleaned up by hexane-acetonitrile partitioning and column chromatography on silica gel. The chlorpyrifos is deteremined by GLC incorporating a flame photometric detector.

TCP

The plant sample is treated with methanol and NaOH at 130°. An aliquot of the methanol is evaporated to near dryness; the residue is taken up in water. Concentrated HCl and salt are added; the freed TCP is extracted into benzene. The benzene extract is chromatographed on an acidic alumuia column using a diethyl ether/pH 6.5 buffer mix for elution. The ether eluate is partitioned with sodium bicarbonate. The bicarbonate solution is acidified and the TCP is extracted into benzene. An aliquot of the benzene solution is silyated with with N,O-bis(trimethylsilyl)acetamide (BSA). The pyridinol trimethylsilyl derivative is then determined by GLC using electron capture detection.

As this method determines total TCP the chlorpyrifos must be determined by an independent method; the TCP is then calculated by difference.

The following check and recovery values are submitted.

plant part	check chlorpyrifos	check TCP	chlorpyrifos fort.(ppm)	chlorpyrifos recovery(%)	TCP fort.(ppm)	TCP recovery(%)
grapes	0.02	0.02	0.1	103	0.2	100
raisins	0.01	0.02	0.1	113	0.2	75
grape pomace	0.08	0.05	0.1	164	0.2	70
juice	0.01	<0.02	0.1	116	0.2	96

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Some of the data submitted with this petition include analyses in which only the total TCP (expressed as parent) was determined. We had earlier agreed to this method of determing residues as it would be simpler for IR-4 to perform although it would also provide a exaggerated value for the combined residues as the molecular weight for TCP (198.4) is less than that for chlorpyrifos (350.6). This method is adequate for gathering residue data. For enforcement purposes, the PAM II method, described first, is adequate.

Residue Data

Residue experiments were carried out in New York and North Carolina. Less than 10% of this country's grapes are grown east of the Rockies; of these ca. 50% are from New York and 1-2% are from North Carolina. Since this use is limited by a label restriction as well as by practicality (the grape root borer isn't found in the West) to the Eastern U.S. we consider the geographic representation of the residue experiments to be adequate.

In both New York and North Carolina the soil around the base of grape vines was treated with 2.25 lb. a.i. (1x) or 4.5 lb. a.i.(2x)/100 gallons of spray. The accompanying table (next page) shows the maximum residues found in these experiments. The New York samples were analyzed for both parent and TCP but are also listed as TCP residues expressed as chlorpyrifos for comparison purposes. In the North Carolina experiments only TCP was determined.

The only residue higher than the proposed tolerance was a 0.82 ppm (TCP was determined but expressed as chlorpyrifos) value which resulted from a 2x application. We do not expect residues in grapes of greater than the proposed tolerance as a result of the proposed use.

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SUMMARY TABLE - RESIDUES OF CHLORPYRIFOS IN OR ON GRAPES AND GRAPE PROCESSING FRACTIONS

LOCATION	APPN DATE	APPN RATE	SAMPLING DATE	FRACTION ANALYZED	MAXIMUM RESIDUES DETECTED (PPM) CHLORPYRIFOS	TCP	TCP RESIDUES EXPRESSED AS CHLORPYRIFOS
FREDONIA, NEW YORK	8/7/79	2.25 1/ lbs.a.i. per 100 gal.	9/26/79 (53 days)	Grapes	0.04	0.06	0.11 2/
				Raisins	0.03	0.03	0.05
				Grape Pomace	0.13	0.08	0.14
				Grape Juice	0.01	0.02	0.04
	"	4.5 lbs.a.i. per 100 gal.		Grapes	0.07	0.05	0.09
				Raisins	0.07	0.04	0.07
				Grape Pomace	0.16	0.09	0.16
				Grape Juice	0.01	0.02	0.04
CLINTON, NORTH CAROLINA	8/6/80	2.25 lbs. a.i. per 100 gal.	9/10/80 (35 days)	Grapes		0.23	0.41
				Grape Pomace		0.02	0.04
				Grape Juice		0.05	0.09
	"	4.5 lbs. a.i. per 100 gal.	"	Grapes		0.46	0.82
				Grape Pomace		0.04	0.07
				Grape Juice		0.02	0.04

1/ Proposed Application Rate

2/ TCP Values converted to chlorpyrifos equivalent by dividing the TCP Value by 0.56

Grapes from each experiment were processed into grape juice and grape pomace (we presume this is wet grape pomace as no drying was indicated). The New York grapes were also processed into byproducts. The highest residues found (TCP expressed as parent) as a result of the proposed use were: raisins, 0.05 ppm; grape pomace 0.14 ppm; and grape juice, 0.09 ppm. The proposed tolerance will accommodate any expected residues in these items.

However residues in dried grape pomace may be higher than those found in wet grape pomace. To determine an appropriate tolerance for dried grape pomace we will use a dry down factor. If wet grape pomace (63% moisture) carrying residues of 0.5 ppm were dehydrated to produce dry grape pomace (9% moisture) the concentration factor would be 2.4x which would result in a residue of 1.2 ppm. We conclude that a tolerance of 2 ppm is needed for dry grape pomace.

Meat, Milk, Poultry and Eggs

Grapes and their byproducts can be used in moderate amounts as livestock feed. A tolerance of 2.0 ppm for the meat, fat, and meat byproducts of cattle is pending (PP#0F2281; this tolerance includes residues realized as the result of a dip treatment). Since the proposed tolerances for grapes and dried grape pomace are no higher than tolerances for other significant feed items (alfalfa hay, 15 ppm, pending; soybean straw, 15 ppm, pending; peanut hulls, 15 ppm; and tomato pomace, 15 ppm, pending) we conclude that the pending 2.0 ppm tolerance for cattle is adequate.

By similar reasoning we conclude that the pending tolerance for milk fat (0.50 ppm reflecting no more than 0.02 ppm in whole milk) is adequate.

For the meat, fat, and meat byproducts of goats, horses, and sheep, tolerances of 1.0 ppm are pending. Based on cattle feeding studies most recently discussed in our review of the 9/10/81 amendment to PP#0F2881 (See memo of 11/6/81, K. Arne) we do not anticipate that the proposed tolerance would be exceeded should treated grapes or dried grape pomace be used as feed for these animals.

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Wet grape pomace can be an important feed item for hogs (up to 70% of the diet) and other processing fractions may constitute up to 20% of the diet. Since no residues greater than 2 ppm are expected for these items and since the maximum amount of chlorpyrifos in a hogs diet would result from feeding 50% alfalfa hay (tolerance-15 ppm) and 50% corn forage and fodder (tolerance-10 ppm) we do not expect that the feeding of grape processing fractions to hogs will have a significant effect on secondary residues. The pending tolerance of 0.5 ppm for the meat, fat and meat byproducts of hogs is adequate.

Grape processing byproducts can comprise 30% of the diet of poultry. The maximum chlorpyrifos in a poultry diet would be expected from the following:

	tolerance (ppm)	% in diet	ppm in diet
alfalfa seeds	15	2.0	3.0
corn grain	0.1	30	.03
cull grapes	0.5	30	.15
soybeans	0.5	20	.10
			3.3

In a poultry feeding study maximum residues of 0.24 and 0.84 ppm were found in the kidney at feeding levels of 3 and 10 ppm, respectively. Combined residues of chlorpyrifos and TCP did not exceed 0.17 ppm in any other tissues. No residue was detected in eggs at either feeding level. Based on these studies we do not expect that pending tolerances for poultry (0.5 ppm) and eggs (0.1 ppm) will be exceeded should treated grape byproducts be used as poultry feed.

TS-769:RCB:K.Arne:MCH:CM#2:RM810:X77377:3/24/82
cc: RF, Circu., K. Arne, Thompson, TOX, EEB, EFB, FDA, PP#2E2584
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