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

MAR 5 1982

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#2F2588/2H5326. Chlorpyrifos on sunflowers. Evaluation of residue data and analytical method

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and
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THRU: Charles L. Trichilo, Chief
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Dow Chemical Company proposes tolerances for the residues of chlorpyrifos (which include the parent plus a metabolite, 3,5,6,-trichloro-2-pyridinol(TCP)) in or on sunflower seeds at 0.2 ppm. A food additive tolerance is proposed on sunflower hulls at 0.5 ppm.

Several chlorpyrifos tolerances are established ranging from 0.01 ppm for eggs and poultry to 15 ppm for peanut hulls (40 CFR 180.342). Many petitions are pending.

Conclusions

1. The nature of the residue is adequately understood. The residue of concern consists of chlorpyrifos plus TCP.

2. Adequate analytical techniques are available for enforcement purposes.

3a. Combined residues of chlorpyrifos and TCP resulting from the proposed use may exceed the proposed tolerance (0.2 ppm) for sunflower seeds. A tolerance of 0.25 ppm would be adequate and should be proposed.

3b. Residues in sunflower hulls will not exceed the proposed tolerance (0.5 ppm) as a result of the proposed use.

3c. Residues in meal, oil, and soapstock will not exceed the proposed tolerance for sunflower seed; food additive tolerances are not needed for these commodities.

4. Existing or pending tolerances for meat, milk, poultry and eggs will accommodate any secondary residues added by the proposed use.

5. An International Residue Limit Status sheet is attached. There is no Codex MRL for chlorpyrifos on sunflowers above step 6.

Recommendations

Toxicological and EFB considerations permitting we recommend for the proposed tolerance on sunflower hulls. We recommend against the proposed tolerance for sunflower seeds; a tolerance of 0.25 ppm would be adequate and should be proposed.

Detailed Considerations

Formulation

The formulations of chlorpyrifos intended for use on sunflowers are Lorsban 4E, an emulsifiable concentrate containing 4 lb a.i./gal, and Lorsban 15G, a granular formulation containing 15% chlorpyrifos. The inert ingredients in both formulations are cleared under Section 180.1001(c). The [redacted] in Lorsban 15G is cleared under Section 180.1001(d).

The manufacturing process was discussed in our review of PP#4F1445 (memo of A. Smith, 5/3/74). The impurities [redacted] in the technical material are [redacted] The remainder, the non-volatiles [redacted] consists of at least seven compounds. We do not expect the impurities in Lorsban® to present a residue problem.

Proposed Use

Chlorpyrifos is to be used to control various pests infesting sunflowers including cutworms, grasshoppers, stem weevils, and sunflower moths. Lorsban 15G is to be applied in a 7 inch wide band over the row and incorporated into the top one inch of the soil. The rate is 1.2 ounces chlorpyrifos per 1,000 linear feet of row (equivalent to 8 ounces of Lorsban 15G per 1000 ft of row or 1.3 lb a.i./A based on a 30 inch row spacing). Lorsban 15G is to be applied no more than once per season.

Lorsban 4E is to be applied as a broadcast foliar spray by air or ground equipment at the rate of 0.5 to 1.5 lb a.i./A (1 to 3 pints product /A). No more than 9 pints (4.5 lb a.i./A) are to be applied per season. The PHI is 42 days. Livestock are not to be grazed in treated areas.

Nature of the Residue

Plant

No metabolism studies were submitted with this petition.

The metabolism of radiolabeled chlorpyrifos (^{14}C and ^{36}Cl) has been studied in corn and bean plants (PP#3F1306). These studies show that chorpyrifos is translocated only to a limited degree from soil or from treated leaves. Chlorpyrifos degrades in UV light in the presence of water by dechlorination to form diols and triols which can undergo ring cleavage. Under prolonged irradiation the products were apparently carbon dioxide, ammonium carbonate and sodium chloride.

Plant metabolism (as indicated by the corn and bean studies) is via hydrolysis to ethyl 3,5,6-trichloro-2-pyridylphosphate; 3,5,6-trichloro-2-pyridylphosphate; 3,5,6-trichloropyridinol (TCP); and material postulated to be a TCP conjugate. TCP can undergo dechlorination (as observed in UV degradation) to form diols and triols which can be conjugated or incorporated into natural plant constituents.

More recently, apple and soybean metabolism studies have been submitted and reviewed (PP#OF2281, memo of 7/7/81, E. Leovey). In the apple metabolism study chloropyrifos and TCP were observed as residues at levels of 36.3 and 5.1 - 5.6% respectively. Two metabolites were postulated to be mono-dechlorinated derivatives of chlorpyrifos from GC/MS data. The aqueous layers contained a metabolite designated B (4.9 to 5.4% of residue) which upon hydrolysis yielded TCP. The hydrolyzed insoluble material yielded metabolites C (5.2-5.7%), D (3.2 to 5.4%) and E (5.5 to 5.7%) which were not characterized due to a lack of sufficient material.

The remainder of the radioactivity was insoluble material (3.3-4.5%) and aqueous layer (1.4-1.5%). The material in the unidentified hydrolyzed fraction consisted of numerous radiolabelled compounds smeared throughout the HPLC fractions. From 90-95% of the radioactivity could be traced; the remainder was probably lost in sample handling.

The ^{14}C residue in soybeans was characterized as 17% incorporated into natural components of the oil; 2.5% chlorpyrifos; 11% TCP; 24% extracted into the aqueous layer and containing at least seven metabolites not hydrolyzable to TPC; 18% solubilized which individually constituted at most 3% of the total residue; 11% in the precipitate and deduced to be incorporated into protein and 8% remaining insoluble, according to our calculations. Unidentified metabolites were claimed to be compounds arising from the plants natural constituents.

In conjunction with PP#s OF2281 and 9F2270 we deferred to Toxicology Branch as to the significance of apple metabolites B, C, D, and E and the unidentified apple and soybean metabolites, particularly the water soluble metabolites. Toxicology Branch has recently concluded (Section 18 by the State of Ohio for Chlorpyrifos on soybeans, memo of 8/11/81, A. Mahfouz) that the unindentified metabolites that are water soluble are not of toxicological significance because water soluble metabolites of organophosphate insecticides are usually inactive degradation products. More recently (memo of 10/28/81, W. Dykstra) Toxicology Branch concluded that the organosoluble metabolites are not of concern. We therefore conclude that the nature of the residue in plants is adequately understood and consists of chlorpyrifos and TCP.

Animal Metabolism

Metabolism in animals has been described in our review of PP#3F1306 (memo of F.D.R. Gee, 3/1/73). In rats, ^{14}C and ^{36}C chlorpyrifos and ^{14}C-TCP were extensively eliminated in the urine and feces. Only 1.1-2.5% of the dose remained in tissues with residues highest in the liver, kidney, stomach and blood. Five ppm chlorpyrifos was fed to a lactating cow for four days. The urinary metabolites were identified as diethylthiophosphate and diethyl phosphate which were 35.9 and 26.8% of the insecticide fed. No chlorpyrifos was found in milk or urine. Approximately 1.7% of the chlorpyrifos fed was found in the feces. Samples were not analyzed for TCP.

Radioactive residues in tissues ranged from 0.01 ppm (bone) to 0.8 ppm (rumen). Residues in milk and muscle were 0.03 ppm; this was considered too low for further analysis. Residues at the 19 ppm feeding level were: fat, 0.10 ppm; liver, 0.22 ppm; and kidney, 0.29 ppm. These residues were considered sufficient for residue characterization and were comparable to the blood levels. Distribution of the dose in urine, feces, gut, tissues and milk was 75.5 and 85.1% 3.5 and 3.7%, 1.2 and 0.6%, 0.7 and 0.8%, and 0.14 and 0.05% at the two feeding levels, 15 and 19 ppm, respectively, for a total of 81 and 90.2%

Urine was acidified and extracted with ether. Metabolites were partitioned into sodium bicarbonate. After acidification, residues were extracted into ether, concentrated, and analyzed by HPLC. TCP constituted at most 15.3% of the urine metabolites. A beta-glucuronide conjugate of TCP was the major urine metabolite, 80-91%. A minor metabolite was tentatively identified as S-ethyl, O-(3,5,6-trichloro-2-pyridyl) phosphorothioic acid. The results shown in the report were for a urine sample collected approximately six days into the diet. Other samples were reported to be similar (W.R. Bauriedil, Dow Chemical, April 27, 1981).

Fat was dissolved in hexane and the ^{14}C-labeled residues reportedly extracted into acetonitrile. After concentration the residue was cleaned up again with a hexane-acetonitrile partition. Solids remaining after hexane dissolution were hydrolyzed. Residues were extracted into ether after acidification and cleaned-up by hexane acetonitrile partition. Chlorpyrifos was the major component (confirmed by GC/MS). It constituted more than 95% of the residue as determined by HPLC, and the remainder was TCP or material, particularly in the solids, which could be hydrolyzed to TCP.

We conclude that the nature of the residue in animals is adequately understood. The residue of concern consists of the 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.

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 determined by GLC incorporating a flame photometric detector.

TCP

The plant sample is treated with methanol and NaOH at 130°C. 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 acidic alumina using a diethyl ether/pH6.5 buffer mix for elution. The ether elute is partitioned with sodium bicarbonate. The bicarbonate solution is acidified and the TCP is extracted into benzene. An aliquot of the benzene solution is silylated with N,O-bis(trimethylsilyl) acetamide (BSA). The pyridinol trimethylsilyl derivative is then determined by GLC using electron capture detection.

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

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The following check and recovery values are submitted

Chlorpyrifos	Check	Recovery Fort. (ppm)	range(%)	avg.(%)
sunflower seeds	<0.01	0.01-0.5	76-110	92
sunflower forage	<0.01	0.01-4.0	76-110	87
sunflower meal	<0.01	0.01-0.05	70-80	77
sunflower hulls	<0.01	0.01-0.05	42-90	66
crude oil	<0.01	0.01-0.05	70-80	75
refined oil	<0.01	0.01-0.05	44-76	56
soapstock	<0.01	0.01-0.05	76-92	83
TCP				
sunflower seeds	0.016	0.05-0.5	72-96	84
sunflower forage	0.022	0.1-2.0	75-98	86
sunflower meal	0.01	0.05-0.2	68-100	85
sunflower hulls	<0.01	0.05-0.2	76-92	87
crude oil	0.014	0.05	60-88	75
refined oil	0.016	0.05-0.2	72-104	88
soapstock	<0.01	0.05-0.2	76-92	83

Adequate analytical techniques are available for enforcement purposes.

Residue Data

Residue experiments were carried out in Michigan, Minnesota, Nebraska, and North Dakota. These data are tabulated on the following page.

State	Plant Part	Application rate (lb. a.i./A) No. of applications 15E	4E	PHI (days)	Residue Chlorpyrifos	TCP	Total
MN	seed	1.4 x 1	1.5 x 2 + 0.5 x 1	65	0.01-0.03	<0.05	0.06-0.08
	seed	1.4 x 1	1.5 x 2 + 0.5 x 3	45	0.02-0.05	<0.05	0.07-0.1
MS	seed	1.2 x 1	1.5 x 2 + 0.5 x 1	65	0.01	<0.05	0.06
	seed	1.2 x 1	1.5 x 2 + 0.5 x 3	44	0.02-0.05	<0.05	0.07-0.1
NB	seed	1.2 x 1	1.5 x 2 + 0.5 x 1	67	0.02-0.05	<0.05	0.07-0.1
	seed	1.2 x 1	1.5 x 2 + 0.5 x 3	46	0.11-0.17	<0.05-0.06	0.16-0.22
ND	seed	1.2 x 1	1.5 x 2 + 0.5 x 1	75	0.03	<0.05	0.08
	seed	1.2 x 1	1.5 x 2 + 0.5 x 3	44	0.09	0.06	0.15
MI	seed	1.2 x 1	1.5 x 2 + 0.5 x 3	42	0.07-0.15	<0.05	0.12-0.20
	seed	1.2 x 1	1.5 x 2 + 0.5 x 1	69	0.01-0.05	<0.05	0.06-0.1
MN	seed	1.4 x 1	0.5 x 2 + 0.5 x 3	45	0.03	<0.05	0.08
	meal	"	"	"	<0.01	<0.05	<0.06
	hulls	"	"	"	<0.06-0.07	<0.05	0.11-0.12
	crude oil	"	"	"	0.01-0.03	<0.05	0.06-0.09
	refined oil	"	"	"	<0.01	<0.05	<0.06
	soapstock	"	"	"	<0.01-0.01	<0.05	<0.05-0.05

These data indicate that the proposed tolerance for sunflower seeds may be exceeded by the proposed use. Residues as a result of the proposed use reached levels of about 0.2 ppm. We therefore recommend that a tolerance of 0.25 be proposed for sunflower seeds. The only processing fraction that showed any concentration of residues was hulls which carried about 2x the residue in the seeds. The proposed tolerance (0.5 ppm) is adequate. No tolerances are required for the remaining process fractions.

Meat, Milk, Poultry and Eggs

Sunflower meal, forage and hulls can be used as livestock feed items. The proposed label includes a label restriction prohibiting the use of forage as feed for livestock. Since the tolerance for hulls is low relative to other feed items for which tolerances are established or pending (alfalfa hay, 15 ppm, pending; citrus pulp, 15 ppm; soybean straw, 15 ppm pending; peanut hulls, 15 ppm; dry tomato pomace, 35 ppm, pending) we do not expect the proposed use to result in secondary residues higher than established or pending meat and milk tolerances (2.0 for the meat fat and meat byproducts of cattle; 1.0 ppm for the meat fat and meat byproducts of sheep; 0.5 ppm for the meat fat and meat byproducts of hogs; 0.50 ppm for milk fat (reflecting no more than 0.02 ppm in whole milk); see PP#OF2281, memo of 11/6/81, K. Arne).

Sunflower meal is a minor feed item for poultry, up to 15% of the diet and could add up to ca. 0.04 ppm chlorpyrifos to that diet. Since this is a minor feed item carrying relatively low residues as compared to other feed items we do not anticipate this use will cause either the existing or pending tolerances (PP#OF2281) for poultry tissue (0.5 ppm) and eggs (0.1 ppm) to be exceeded.

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