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

DEC 15 1983

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP# 3F2957 Metolachlor on stone fruits. Evaluation of analytical methods and residue data.
Accession numbers 071926 and 071927

FROM: K. H. Arne, PhD., Chemist
Residue Chemistry Branch
Hazard Evaluation Division (TS-769)

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

TO: Richard Mountfort, PM Team No. 23
Registration Division (TS-767)
and
Toxicology Branch
Hazard Evaluation Division

Ciba-Geigy Corporation proposes tolerances for residues of the herbicide metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide] and its metabolites determined as 2-[(2-ethyl-6-methylphenyl)amino]-1-propanol (CGA-37931) and 4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholinone (CGA-49751), each expressed as parent, on stone fruits at 0.1 ppm.

Metolachlor tolerances are established for several RAC's at levels ranging from 0.02 ppm for meat, milk, poultry, and eggs to 3.0 ppm for peanut forage and hay. Several tolerances are pending including those for the liver and kidneys of cattle, horses, goats, hogs, and sheep (PP#2F2720)

Conclusions

1. The nature of the residue in both plants and animals is adequately understood. The residue of concern consists of parent plus 2-[(2-ethyl-6-methylphenyl)amino]-1-propanol (CGA-37913) and 4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholinone (CGA-49751).

2. A label restriction that prohibits the grazing of livestock on treated orchard floors is needed.

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

4. The methods used to determine residues of simazine resulting from metolachlor-simazine tank-mix appications are adequate for collection of residue data.

5. The proposed tolerance (0.1 ppm) will not be exceeded by the proposed use.

6. The proposed tank mixes with paraquat and glyphosate will not cause the existing tolerances for these herbicides to be exceeded. (Paraquat tolerances are established for peaches, necatarines, plums, apricots and cherries, all at 0.05 ppm; a group tolerance for glyphosate on stone fruits is established at 0.2 ppm)

7. There are no tolerances established for simazine on nectarines or apricots, but tolerances of 0.25 ppm are established for cherries, peaches, and plums. The petitioner should revise Section B so that it is clearly stated that tank mixes of metolachlor plus simazine are not permitted on nectarines and apricots. Likewise, the suggested sequential use of simazine should be excluded from apricots and nectarines.

8. Since no feed items are involved, there will be no problem of secondary residues in meat, milk, poultry, and eggs.

9. There are no Codex, Mexican, or Canadian tolerances for metolachlor on stone fruit. Thus the question of compatibility does not arise.

Recommendation

We recommend against the proposed tolerance. For a favorable recommendation we require a revised Section B in which it is clearly stated that a tank mix of metolachlor plus simazine (or any use of simazine) is not allowed on nectarines and apricots.

Detailed Considerations

Manufacture and Formulation

The manufacturing process and the composition of the technical material are discussed on our review of PP#8F2081 (memo of 4/2/79, A. Smith). Technical metolachlor is about 95% pure. The impurities are not expected to present a residue problem.

The formulation of metolachlor proposed for use on sorghum is Dual 8E, and emulsifiable concentrate containing 8 lb a.i./gallon. The inert ingredients are cleared under

180.1001 (c) or (d).

Proposed Use

Metolachlor is to be applied to the floors of stone fruit orchards at rates of up to 4.0 lb. a.i./A in the Spring when weeds are not present. For control of broadleaf weeds not lis3ed on the Dual 8E label, metolachlor may be tank mixed at the above rates with 1-4 lb. a.i./A simazine, depending on the crop, to weed free soil. In the event that weeds are present metolachlor alone or in a tank mix with simazine may sequentially follow an application of paraquat or glyphosate or metolachlor alone or in mixtures with simazine may be applied in tank mixture combinations with paraquat or glyphosate. Paraquat may be applied at rates of 0.5-1.0 lb. a.i./A. Glyphosate may be applied at rates of 1-5 lb a.i./A, depending on the weed species.

To prevent livestock from ingesting excessive residues of metolachlor the petitioner should add a label restriction prohibiting food animals from grazing on treated orchard floors.

Tolerances are established for paraquat on cherries, apricots, plums, peaches, and nectarines, all at 0.05 ppm (N). For glyphosate a stone fruit group tolerance is established at 0.2 ppm. Simazine tolerances are established for cherries, peaches, and plums, all at 0.25 ppm, but no tolerances are established for apricots and nectarines. Therefore the proposed tank mix or any other use of simazine on apricots and nectarines cannot be approved. This problem could be resolved by the establishment of a simazine stone fruit group tolerance but the recently completed simazine registration standard recommends against this option until gaps in peach residue data and residue data for the chlorometabolites of simazine on plums and cherries are submitted. The petitioner should therefore revise Section B in such a way that it is clear that applications of simazine to apricot and nectarine orchards are not permitted.

Nature of the Residue

Studies designed to determine the metabolism of metolachlor in corn and soybeans were submitted with PP#s 5G1553, 6F1606, and 6G1708 and were discussed in our reviews of those petitions. In both soybeans and corn the major metabolic pathway involves conjugation with glutathione, formation of the mercaptan, conjugation of the mercaptan with glucuronic acid, hydrolysis of the methyl ether and conjugation of the alcohol with a neutral sugar.

Animal metabolism studies have been carried out in rats and goats using ^{14}C labeled metolachlor and in goats only using ^{14}C biosynthesized metabolites. These studies were discussed in our review of PP#5G1553 (memo of 2/12/74, D. Reed). They show that metolachlor is rapidly eliminated with only trace residues

remaining in tissue (liver). Comparison of the urine metabolites with those found in corn indicates that, although the conjugating natural compounds are different, the hydrolyzed pesticide moieties are similar in plants and animals. The significant components of the residue consist of the parent and two of its metabolites: 2-[(2-ethyl-6-methylphenyl)amino]-1-propanol (CGA-37931) and 4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholinone (CGA-49751). The analytical method determines these components and their conjugates.

We conclude that the metabolism of metolachlor in plants and animals is adequately understood.

Analytical Methods

The method used to collect residue data (Ciba-Geigy method AG-338) is a variation of Analytical Method AG-286, which has undergone a successful method trial (PP#5F1506, memos of 7/28/76 and 7/29/76, R.R. Watts). The method involves the hydrolysis (refluxing overnight with 6N hydrochloric acid) of metolachlor, its conjugates, and metabolite residues to CGA-37913 and CGA-49751, which are then determined separately.

CGA-49751 is partitioned into dichloromethane from an aliqout of the acid extract. The dichloromethane phase is washed with 5% sodium carbonate then chromatographed on 16% moisture silica gel. The CGA-49571 is then converted to the chloroethanol derivative which is partitioned into hexane and then cleaned up on a 16% moisture silica gel column. Quantitation is by GC equipped with a Dohrmann microcoulometric detector in the nitrogen mode.

CGA 37913 is partitioned into hexane from a second aliquot of the hydrolysis mixture which had been made basic with 50% sodium hydroxide solution. The hexane portion (containing the CGA 37913) is chromatographed on an 18% moisture alumia column, then on a silica gel column. Quantitation is by GC equipped with a Hall electrolytic conductivity detector specific for nitrogen.

The following recovery values are submitted:

	CGA-37913			CGA-49751		
	fort.(ppm)	rec.(%)	avg.	fort.(ppm)	rec.(%)	avg.
cherries	0.03-0.4	94-113	104	0.05-0.5	84-115	100
peaches	0.03-0.5	77-95	86	0.05	86-88	87
plums	0.03-0.5	90-102	96	0.5	85	-
dried plums	0.5	78	-	0.05-0.5	76-130	103
apricots	0.03-0.5	64-93	78	0.5	100	-
dried apricots	0.5	90	-	0.05-0.5	110-114	112

No residues (<0.03 ppm CGA 37014, <0.05 ppm CGA 49751) were detected in any control samples. We conclude that adequate analytical methods are available for enforcement of the proposed tolerance.

This petition includes residue data for tank mixes of metolachlor plus simazine. Simazine residues were determined by Ciba-Geigy Methods AG-295, which determines parent plus its monodealkylated metabolite, and AG-281, which determines the di-dealkylated metabolite. These or similar methods have been successfully tried out and are suitable for collection of residue data.

Adequate (PAM II) methods are available for enforcement of existing paraquat, glyphosate, and simazine tolerances.

Residue Data

Residue experiments were carried out on apricots (CA), cherries (CA, WA, MI), prunes (CA), and peaches (CA, PA, TN). Metolachlor was applied between February and May, in most intances during April, at rates of 4.0 (1x) or 8.0 (2x) lb. a.i./A. The mature fruit was sampled at harvest, 46 to 216 days later. No residues of either CGA-37913 (<0.03 ppm) or CGA-49751 (<0.05 ppm) were detected in any samples. These data adequately support the proposed tolerance, 0.1 ppm.

In three peach experiments simazine was tank-mixed with metolachlor at rates of 2 (1x) or 4 (2x) lb. a.i./A. No residues of simazine (<0.2 ppm) were detected at harvest, 75-162 days later. Based on these data and since the proposed tank mixes are at rates already registered for simazine (except as noted under proposed use, above), glyphosate, and paraquat, we conclude that the existing tolerances for these herbicides are adequate.

Meat, Milk, Poultry, and Eggs

Since no feed items are involved there will be no problem of secondary residues in meat milk poultry and eggs.

Other Considerations

There are no Codex, Mexican, or Canadian tolerances established for metolachlor on stone fruits; thus the question of compatability does not arise.

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Metolachlor PETITION NO 3F2957

CCPR NO. _____

F. L. 11/15/93

Codex Status

[✓] No Codex Proposal Step 6 or above

Residue (if Step 9): _____

Crop(s) Limit (mg/kg)

Proposed U. S. Tolerances

Parent plus 2-[(2-ethyl-6-methylphenyl)amino-1-propanol and 4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholinone

Residue:

Crop(s) Tol. (ppm)

stonefruit 0.1 ppm

CANADIAN LIMIT

Residue: _____

Crop Limit (ppm)

none (on stone fruit)

MEXICAN TOLERANCIA

Residue: _____

Crop Tolerancia (ppm)

none

Notes: