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

MAR 6 1984

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: EPA Accession Number 072161
EPA Accession Number 072162
PP4F3000: Metolachlor in or on Apples.
Evaluation of analytical method and residue data.

TO: R. Mountfort, PM 23
Registration Division (TS-767)

and

Toxicology Branch
Hazard Evaluation Division (TS-769)

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

FROM: R. W. Cook
Residue Chemistry Branch
Hazard Evaluation Division (TS-769)

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-morpholine (CGA-49751), each expressed as parent, on apples at 0.1 ppm.

Tolerances for residues of metolachlor have been established under 40 CFR 180.368 at levels from 0.02 ppm for meat, fat, meat byproducts, poultry, and eggs to 3 ppm for peanut forage and hay. Several tolerances are pending, including PP2F2720 (liver and kidney of cattle, goats, hogs, horses, and sheep), PP3F2957 (stone fruit), and PP3F2958 (tree nuts).

Conclusions:

1. The nature of the residue is adequately understood in plants and animals. The residue of concern consists of the parent compound metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl-N(2-methoxy-1-methylethyl)acetamide] plus 2-[(2-ethyl-6-methylphenyl)amino]-1-propanol (CGA-37931) and 4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholine (CGA-49751).

2. A label restriction against the grazing of livestock on treated orchard areas is needed.

3. Adequate analytical methods are available for enforcement purposes.

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

5. The proposed 0.1 ppm tolerance on apples is not likely to be exceeded as a result of the use as proposed. Residues of metolachlor in dry apple pomace are likely to exceed 0.1 ppm; a level of 0.5 ppm would be appropriate. The petitioner should propose a feed additive tolerance at this level.

6. The proposed tank mixtures with paraquat and glyphosate will not cause the existing tolerances for these chemicals to be exceeded. Tolerances for residues of paraquat dichloride are established in apples at 0.05 ppm (N); glyphosate tolerances are 0.2 ppm in pome fruit; and simazine tolerances in apples are 0.25 ppm.

7a. Secondary residues in meat or milk would be adequately covered by the existing meat and milk tolerances.

7b. There will be no problem of secondary residues in poultry tissue or eggs since there are no poultry feed items involved.

8. There are no Codex, Mexican, or Canadian tolerances for metolachlor on apples, and no compatibility problem is anticipated.

Recommendation

We recommend against the proposed tolerance, for the reasons cited in 2 and 5 above. For a favorable recommmendation the petitioner should be informed of the following:

1. A label restriction prohibiting the grazing of livestock animals in treated orchard areas is needed.

2. A feed additive tolerance of 0.5 ppm for residues of metolachlor and its metabolites in dry apple pomace should be proposed.

DETAILED CONSIDERATIONS:

Manufacture and Formulation:

We have previously concluded that the impurities in technical metolachlor are not likely to cause a residue problem (A. Smith, 4/2/79, PP 8F2081). The metolachlor formulation proposed for use on apples is Dual 8E, an emulsifiable concentrate containing 8 pounds active ingredient per gallon. The inerts in this formulation are cleared under 40 CFR 180.1001.

Proposed Use:

Dual 8E is applied to the floor of apple orchards at 1 to 2 quarts per acre (2 to 4 lbs. a.i. metolachlor/A) in a minimum of 10 gallons water in the spring when weeds are not present. For control of additional broadleaf weeds, tank mix at the above rates with 2 to 4 lbs. a.i/A of simazine and apply to weed free soil. If weeds are present, metolachlor alone or in tank mix with simazine may sequentially follow or may be tank mixed with paraquat or glyphosate. Paraquat may be applied at 0.5 to 1.0 lbs. a.i./A and glyphosate at 1 to 5 lbs. a.i./A. Keep spray off foliage and stems of trees to avoid excessive residues or possible foliar injury.

As suggested in PP 3F2957, a label restriction prohibiting the grazing of livestock animals in treated orchard areas is needed.

Tolerances are established at 0.05 ppm for negligible residues of paraquat dichloride in apples under 40 CFR 180.205; for residues of simazine at 0.25 ppm in apples under 180.213; and for residues of glyphosate under 180.364 in pome fruits at 0.2 ppm.

Nature of the Residue:

The nature of the residue has been extensively discussed in our previous reviews of subject chemical. We have previously concluded (5G1553, 6F1606, 6G1708, 3F2957, 3F2958) that the major metabolic pathway in corn and soybeans lies in conjugation with glutathione, formation of the mercaptan, conjugation of the mercaptan with glucuronic acid, hydrolysis of the methyl ester and conjugation of the alcohol with a neutral sugar. (K. Arne, PP3F2957, 12/15/83). Animal metabolism studies have also been discussed previously. The prime disucussion is located in D. Reed memo of 2/12/74, PP5G1553. Metolachlor is rapidly eliminated in rats and goats with liver as the tissue containing residues at trace levels. These studies have also shown that while the urine metabolites are conjugated by different natural compounds than found in corn conjugated residues, the hydrolyzed moieties derived from the parent pesticide are similar in plants and animals. (K. Arne, PP3F2957, 12/15/83). The residue of concern consists of the parent compound metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl-N-(2-methoxy-1-methylethyl)acetamide] and its metabolites 2-[(2-ethyl-6-methylphenyl)amino]-1-propanol (CGA-37931) and 4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholine (CGA-49751). These compounds and their conjugates are determined by the analytical method.

Analytical Method:

Method AG-338, a modification of Method AG-286, was used to determine residues of metolachlor in apples and apple fractions. Method AG-286 has been successfully tried in EPA laboratories (PP 5F1506, R. R. Watts, 7/28/76, and 7/29/76). In principle, metolachlor and its metabolites and conjugates are hydrolyzed by reflux with 6N hydrochloric acid to CGA-37913 and CGA-49751 for determination as separate compounds under different GC conditions. Details of the

procedure may be found in our previous reviews of PP3F2957 and PP3F2958. Recoveries of the metolachlor metabolites CGA-37913 and CGA-49751 at fortification levels of 0.02 - 0.5 ppm and 0.04 - 0.5 ppm ranged from 76 - 132% and 53 - 114%, respectively. Recoveries of simazine and its metabolites G-28279 and G-28273 at fortification levels of 0.05, 0.05 ppm and 0.1 - 0.5 ppm ranged from 69 - 109%, 57 - 105%, and 93 - 111%, respectively. Methods are available in PAM II for enforcement of simazine, paraquat, and glysphosate tolerances.

We conclude that adequate analytical methods are available for enforcement purposes.

Residue Data:

Residue trials were conducted on apples grown in NY, MI, CA, and WA. According to Agricultural Statistics (1979), these four states account for 61% of the apples produced. Thus, the geographical representation is adequate. Metolachlor as the Dual 8E formulation was applied in the spring at 4 lbs. a.i./A and at 2X (8 lbs. a.i./A). Tank mixture of metolachlor and simazine at 4 + 4 lbs. a.i./A also applied. Mature fruit samples obtained at 102 to 178 days after treatment and analyzed by the above method.

No detectable residues of CGA-37913 (<0.03 ppm) or CGA-49751 (<0.05 ppm) were found in fresh apples as a result of either normal or 2X application rate and applied alone or in tank mixture with simazine, except one unwashed fresh apple treated at 2X showed 0.06 ppm of CGA-49751.

Treated fresh apples were commercially processed at Musselman's into washed fresh apples, sliced apples, peels and cores, sauce, juice, and wet pomace. Dry pomace made by laboratory drying of wet pomace samples. With the exception of dry pomace, no detectable residues of CGA-37913 (<0.03 ppm) or CGA-49751 (<0.05 ppm) were found in processed apples. One dry pomace sample receiving 2X treatment rate showed 0.03-0.05 ppm of CGA-37913.

Other dry pomace samples found to contain 0.21 to 0.29 ppm of CGA-37913 only and no detectable residue (<0.05 ppm) of CGA-49751 were considered suspicious by the petitioner. The petitioner's conclusions are based upon plant metabolism studies showing that both CGA-37913 and CGA-49751 are expected, and method validation studies showing CGA-37913 as the only compound produced when parent metolachlor is analyzed by the enforcement method. Therefore, additional 'tree-picked' apples obtained at the same time and from the same trees were processed into dry pomace. These 'treepicked' dry pomace samples showed no detectable residues of CGA-37913 or CGA-49751.

The petitioner, for supporting data, submits studies showing that other uses of metolachlor on stone fruits (apricot, cheery, prune, and peach) similarly showed non-detectable residues. PP 3F2957, metolachlor on stone fruit, is currently in reject status,

but we did conclude therein that residues of metolachlor in stone fruits are not likely to exceed the proposed 0.1 ppm tolerance.

We would expect that apples for processing are likely to be harvested from the ground, i.e. not "wholly tree-picked" and therefore may contain metolachlor residues at the levels indicated in these studies. Based upon these data, we expect that a feed additive tolerance of 0.5 ppm in dry apple pomace would be adequate. The petitioner should proposed such a tolerance.

We conclude that metolachlor residues in or on the raw agricultural commodity apples are not likely to exceed the proposed 0.1 ppm tolerance.

Meat, Milk, Poultry, and Eggs:

There will be no problem of secondary residues in poultry tissue or eggs since there are no poultry feed items involved.

The only feed item of concern is apple pomace which may be fed to livestock at rates up to 50%. Feeding studies were conducted in conjunction with PP 5F1606. Cattle fed at up to 5 ppm of metolachlor showed residues less than method sensitivity in milk (<0.006 ppm CGA-37913 and <0.01 ppm CGA-49751) and meat (<0.02 ppm CGA-37913 and <0.04 ppm CGA-49751).

No detectable residues were found in fresh apples and wet pomace, and considering the recommended for feed additive tolerance of 0.5 ppm in dry apple pomace, any secondary residues in meat or milk would be adequately covered by the existing meat and milk tolerances.

OTHER CONSIDERATIONS:

International Tolerances:

There are no Codex, Mexican, or Canadian tolerances established for metolachlor, and therefore, the question of compatibility does not arise. An International Residue Limit Status sheet is attached.

Removal of Residues:

The petitioner states that removal of residues is not necessary since no residues in excess of the proposed tolerance are contemplated.

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Metolachlor

PETITION NO. 4F3000

CCPR NO. none

R. W. Cook
2/16/84

F. L. 2/16/84

Codex Status

[X] No Codex Proposal Step 6 or above

Proposed U.S. Tolerances

Metolachlor
[2-chloro-N-(2-ethyl-6-methylphenyl
-N-(2-methoxy-1-methylethyl)acetamide]
plus
2-[(2-ethyl-6-methylphenyl)amino]-1-propanol
and
4-(2-ethyl-6-methylphenyl)-2-hydroxy-
5-methyl-3-morpholine

Residue (if Step 9):

Residue: (above)

Crop(s)	Limit (mg/kg)

Crop(s)	Tol. (ppm)
Apples	0.1

CANADIAN LIMIT

Residue:

Crop	Limit (ppm)
none	(on apples)

MEXICAN TOLERANCIA

Residue:

Crop	Tolerancia (ppm)
none	

Notes: Each metabolite expressed as parent.