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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

PP# 3F2958 Metolachlor on tree nuts. Evaluation of analytical method and residue data.
Accession numbers 071928 and 071929

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Ciba-Geigy Corporation proposes tolerances for residues of the herbicide metolachlor [2-chloro-N-(2-methyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide] and its metabolites determined as 2-[(2-ethyl-6-methylphenyl)amino]-1-propanol (CGA-37913) and 4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholinone (CGA-49751), each expressed as parent compound, as follows:

Nutmeats	0.1 ppm
Almond shells	0.1 ppm
Almond hulls	0.3 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 (40 CFR 180.368). 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 prohibiting 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 applications are adequate for collection of residue data.

5. The proposed tolerances will not be exceeded by the proposed use. However, a tolerance should be proposed for tree nuts instead of nutmeats, and the proposed 0.1 ppm tolerance for almond shells should be deleted in a revised Section F.

6. The proposed tank mixes with paraquat and glyphosate will not cause the existing tolerances for these herbicides to be exceeded. (A crop group tolerance for paraquat on nuts is establisheed at 0.05 ppm; a crop group tolerance for glyphosate on nuts is established at 0.2 ppm)

7. There are no tolerances established for simazine on beechnuts, cashews, chestnuts, chinquapins, butternuts, Brazil nuts or hickory nuts, but tolerances of 0.25 ppm are established for walnuts, almonds, pecans, filberts, and Macadamia nuts. The petitioner should revise Section B so that it is clearly stated that tank mixes of metolachlor plus simazine are not permitted on those nuts for which tolerances are not established. Likewise, the suggested sequential use of simazine should be excluded from these crops.

8. Almond hulls can be used as a feed item for meat and dairy animals but since higher tolerances than those proposed for these items are established for more significant feed items (i.e., peanut hay, 3.0 ppm and soybean hay, 2.0 ppm) the added potential for secondary residues in meat and milk as a result of the proposed use is not significant.

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

10. There are no Codex, Mexican, or Canadian tolerances for metolachlor on tree nuts. Thus the question of compatibility does not arise.

Recommendations

We recommend against the proposed tolerances. For a favorable recommendation we require a revised Section B in which it is made clear that the proposed tank mixes and

sequential treatments of metolachlor plus simazine are not allowed on those nut crops for which simazine tolerances are not established (beechnuts, cashews, chestnuts, chinaquapins, butternuts, Brazil nuts, and hickory nuts). We also require a label restriction that prohibits livestock from grazing on treated orchard floors. Finally, a tolerance should be proposed for tree nuts instead of nutmeats, and the proposed 0.1 ppm tolerance for almond shells should be deleted in a revised Section F.

Detailed Considerations

Manufacture and Formulation

The manufacturing process and the composition of the technical material are discussed in 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, an 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 tree nut orchards (almonds, butternuts, beechnuts, Brazil nuts, cashews, chestnuts, chinquapins, filberts, hickory nuts, Macadamia nuts, pecans, and walnuts) 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 listed 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, and applied 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.

A group tolerances is established for paraquat on nuts at 0.05 ppm (N). A group tolerances for glyphosate on nuts is established at at 0.2 ppm. Simazine tolerances are established for walnuts, almonds, pecans, filberts, and Macadamia nuts, all at 0.25 ppm, but no tolerances are established for beechnuts, cashews, chestnuts, chinquapins, butternuts, Brazil nuts, and hickory nuts. Therefore the proposed tank mix or any other use of simazine on beechnuts, cashews, chestnuts, butternuts, Brazil nuts, and hickory nuts cannot be approved. This problem could be resolved by the establishment of a simazine

tree nut group tolerance but the recently completed simazine registration standard recommends against this option until residue data for the chlorometabolites of simazine on the representative commodities (almonds, walnuts, and pecans) are submitted. The petitioner should therefore revise Section B in such a way that it is clear that applications of simazine to beechnuts, cashews, chestnuts, chinquapins, butternuts, Brazil nuts, and hickory nuts are not allowed.

Also, to remove the possibility of illegal secondary residues in meat and milk that could result from livestock grazing on treated orchard floors, the petitioner should revise Section B to include a grazing restriction.

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 tissues (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-37913) 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 (boiling 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.	Recovery	Avg.	Fort.	Recovery	Avg.
Almonds	0.03-0.5	80-82%	81	0.05-0.1	79-88%	85
hulls	0.03-0.5	60-80%	70	0.05-0.5	56-70%	63
shells	0.03-0.1	59-83%	71	0.05-0.1	95-96%	96
Walnuts	0.03	113%	--	0.5	72	--
shells	0.1	75%	--	--	--	--
Pecans	0.03	67	--	0.1	86	--
shells	0.1	85	--	--	--	--

No residues (<0.03 ppm CGA-37913, <0.05 ppm CGA-49751) were detected in any control samples of nuts, shells, or hulls. 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 determined 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 almonds (CA), walnuts (CA,), and pecans (SC, MS). Metolachlor was applied between February and May, in most instances during April, at

rates of 4.0 (1x) or 8.0 (2x) lb. a.i./A. At harvest, 123-243 days later, no residues of either CGA-37913 (<0.03 ppm) or CGA-49751 (<0.05 ppm) were detected in any nut samples. In almond hulls, combined residues of metolachlor were as high as 0.25 ppm; in almond shells, to 0.09 ppm. These data support the proposed tolerances for nutmeats (0.1 ppm) and almond hulls (0.3 ppm). However, the tolerance for nutmeats should be expressed as tree nuts. No tolerances are needed for almond shells since the shells of nuts are not considered to be part of the RAC.

In three experiments (one each on walnuts, almonds, and pecans) 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, 123-188 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

Almond hulls can be used as a livestock feed item, up to 25% of the diet for beef and dairy cattle, to 50% of the diet for sheep (finishing lambs), less for others. However, since higher tolerances than those proposed here are established for more significant feed items, peanut forage (3.0 ppm) and soybean forage (2.0 ppm), the proposed use will not increase the potential for secondary residues in meat and milk.

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

Other Considerations

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