

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

JUL 17 1981

**OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES**

Memorandum

SUBJECT: PP#1F2521. Metolachlor in Corn. Evaluation of analytical method and residue data.

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The CIBA-GEIGY Corp., proposes tolerances for residues of the herbicide metolachlor, 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide, and its metabolites, (each expressed as metolachlor), 2-[(2-ethyl-6-methylphenyl)amino]1-propanol and 4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholinone as follows:

Fresh corn including sweet corn (kernels plus cobs, husks removed)	0.1 ppm
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Popcorn grain 0.1 ppm

Permanent tolerances are established for metolachlor (§180.368) in corn grain (except popcorn) at 0.1 ppm; soybeans at 0.1 ppm, and eggs, milk, and the meat, fat, and meat byproducts of livestock at 0.02 ppm; peanuts at 0.1 ppm, peanut hulls at 1.0 ppm; and peanut forage and hay at 3.0 ppm (PP#9F2213); sorghum grain at 0.3 ppm and fodder at 2.0 ppm; and corn forage and fodder at 1 ppm.

Tolerances are pending for metolachlor in sunflower seed at 0.3 ppm (PP#0E2461), flax at 0.2 ppm (PP#0E2417), cottonseed at 0.1 ppm (PP#1F2506), and seed and pod vegetables at 0.3 ppm (PP#1F2495).

Conclusions

1. The nature of the residues in plants and animals is adequately understood. The significant components of the residues are the parent metolachlor and its metabolites as noted above.

2. Adequate analytical methods are available for enforcement purposes.
- 3a. Residues of metolachlor in fresh corn and popcorn grain are not likely to exceed the proposed tolerances.
- 3b. Residues of metolachlor in corn fodder and forage are not likely to exceed the established tolerance from the proposed and registered uses.
- 3c. Residues of the various compounds (atrazine, cyanazine, dicamba, glyphosate, paraquat simazine) proposed for tank-mix uses or uses following metolachlor are not likely to exceed the established tolerances.
4. Residues of metolachlor could occur in eggs, milk, and meat of livestock [§180.6(a)(2)]. However, such residues would be covered by the established tolerances.

Recommendation

TOX and EFB considerations permitting, We recommend for the proposed tolerances at 0.1 ppm on fresh corn (including sweet corn) and on popcorn. We definite to EFB on the adequacy of the crop rotation restrictions.

DETAILED CONSIDERATIONS

Proposed Uses

Metolachlor, formulated as Dual 8E (8 lb act/gal.), is proposed for preplant, preemergence, or early postemergence application for grass and weed control in corn.

Metolachlor alone: apply either preplant or preemergence at rates of 1.5-3.0 lb act/A depending on the soil type.

Combinations

Tank-mixtures

Apply metolachlor (1.25-2.5 lb act/A) plus atrazine or simazine (either at 1-2 lb act/A) preplant or preemergence depending upon the soil type. The following tank-mix application may be applied in lieu of the above: 1.25-2.5 lb metolachlor/A plus 0.5-1.0 lb atrazine/A plus 0.5-1.0 pb simazine/A.

1.5-2.5 lb metolachlor/A plus 1.2-2.0 lb atrazine/A may be applied postemergence. Application is to occur before grass and weeds pass the 2-leaf stage and before corn exceeds 5 inches in height.

Preplant or preemergence applications of 1.25-2.5 lb metolachlor/A plus 0.8-2.5 lb cyanazine/A may be used, depending on the soil type, on field corn and silage corn only.

Preemergence application (on flat-plant field corn, no furrows) of 2.0-2.5 lb metolachlor/A plus 0.5 lb dicamba/A may be used depending on the soil type.

For minimum-tillage or no-tillage systems before, during, or after planting but before corn emerges apply 1.5-2.5 metolachlor/A plus 1.2-2.0 lb atrazine or simazine/A depending on the soil type. As an alternative, 1.5-2.5 lb metolachlor/A plus 0.6-1.0 lb atrazine/A plus 0.6-1.0 lb simazine/A may be used. Apply 0.25-0.50 lb paraquat/A or 1.1-3.0 lb glyphosate/A along with the tank-mixture.

Bicep® 4.5L Herbicide contains, as active ingredients, metolachlor and atrazine (2.5 lb + 2.0 lb act/gal.). The proposed application rates for Bicep is reported to be identical to the metolachlor plus atrazine tank-mixture already discussed. Bicep may be used alone or in tank-mixes with metolachlor, atrazine, or simazine for weed control in conventional tillage corn. Bicep may also be tank-mixed with either paraquat or glyphosate alone or in combination with simazine in minimum-tillage or no-tillage corn.

Bicep may be applied alone as preplant or preemergence at rates of 2.25-4.5 lb act/A (1.25-2.5 lb metolachlor plus 1.0-2.0 lb atrazine) depending on the soil type (same rates as indicated earlier.) Postemergence applications are permitted at the above rates before corn exceeds 5 inches in height.

Bicep combinations

Tank-mixtures with atrazine, simazine, or metolachlor (conventional tillage)

Add up to 1.0 lb atrazine/A to the above proposed Bicep rates. (This would result in a maximum rate of 3.0 lb atrazine/A. For metolachlor, the addition of 0.5 lb act/a would result in the previously maximum proposed rate of 3.0 lb metolachlor when used alone. For simazine add up to 1.0 lb act/A.

Tank-mixtures of Bicep or Bicep plus simazine, with paraquat or glyphosate for minimum-tillage or no-tillage systems

Apply before, during, or after planting, but before corn emerges at combined metolachlor plus atrazine rates of 2.7-4.5 lb act/A (same as for preceding Bicep applications). Up to 1.0 lb simazine/A may be added in the northeastern U.S. Paraquat or glyphosate may be added at respective rates of 0.25-0.50 lb act/A and 1.125 lb act/A.

Registration Uses

Atrazine, 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, is registered for use on corn at 4.0 lb act/A. Preplant, preemergence, or post emergence (3 weeks after emergence) applications are permitted. No grazing or feeding of forage from treated areas to livestock for 21 days after treatment is permitted. A tolerance of 0.25 ppm is established for fresh corn including sweet corn (kernels plus cobs with husks removed), corn grain (includes popcorn), and a tolerance of 15 ppm is established for forage and fodder (§180.220).

Cyanazine (Bladex), 2-[[4-chloro-6-(ethylamino)-s-triazin-2-yl]amino]-2-methyl-propionitrile, is registered for use on corn at 4.0 lb act/A (preemergence) or 2.0 lb act/A (postemergence before the crop reaches the 5-leaf stage). A tolerance of 0.05 ppm is established on corn grain (fresh including sweet: kernels plus cobs with husk removed); and, fodder and forage (§180.307).

Dicamba, 3,6-dichloro-o-anisic acid, is registered for preemergence use at 1.0 lb act/A before the crop is 36 inches tall. Grazing of treated areas is not permitted. Harvesting for dairy animal feed prior to the ensilage stage (milk stage) is not permitted. A tolerance of 0.5 ppm is established for field corn grain and fodder and forage (§180.227).

Glyphosate, N-phosphonomethylglycine, is registered for use on corn for preemergence applications at rates of 1-5 lb act/a.. A total of 8 lbs act/A is not to be exceeded, and feeding or foraging of treated crops within 8 weeks of application is not permitted. A tolerance of 0.1 ppm is established for grain and a tolerance of 0.2 ppm is established for forage (§180.364).

Paraquat, 1,1-dimethyl-4,4'-bipyridinium dichloride, is registered for preplant and preemergence uses at 1.0 lb act/A. A tolerance of 0.05 ppm is established for corn grain, fodder, and forage (§180.205).

Simazine, 2-chloro-4, 6-bis (ethylamino)-s-triazine, is registered for preplant or preemergence applications at 4.0 lb act/A on corn. Grazing of treated areas is not permitted. A tolerance of 0.25 ppm is established on fresh corn including sweet corn (kernels and cobs with husks removed, grain, and fodder and forage (§180.243).

The proposed rates for the various chemicals with registered uses are within the registered rates.

The label bears various crop rotation restrictions. We defer to EFB as to the adequacy of these restrictions to preclude residues in follow-up crops.

The formulations' inert ingredients are cleared for use under §180.1001. The manufacturing process and the composition of technical metolachlor are discussed in PP8F2081. The impurities are not likely to produce a residue problem.

We have considered the question of the possible presence of nitrosoamines in previous memos (PP#7F1913). We concluded that nitrosoamine formation is unlikely.

Nature of the Residue

We have considered the metabolism of metolachlor in plants and animals in previous reviews (PP#7F1913, 6G1708, 6F1606, 5G1553). Plants (corn, soybeans) absorb, translocate and metabolize metolachlor. The primary path of plant metabolism involves hydrolysis and conjugation with plant constituents.

Metolachlor is ingested, metabolized, and rapidly eliminated by animals (rats, goats, cattle, chickens) with some deposition of residues in tissues. While the conjugating natural components in animals differ from these in plants, the metabolic components are similar.

The nature of the residue in plants and animals is similar. The significant components of the residues consist of the parent compound and its metabolites: 2-[(2-ethyl--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.

The nature of the residue is adequately delineated.

Analytical Methods

Metolachlor: a sample is relaxed overnight with dilute hydrochloric acid. (This procedure converts metolachlor, its metabolites, and conjugates to CGA-37913 and CGA-49751). The extract is made basic, and the CGA-37913 is extracted into hexane. This extract is cleaned up on alumina and silica gel columns and concentrated. The CGA-37913 in the concentrate is determined by gas-liquid chromatography (GLC) using an electrolytic conductivity detector which is sensitive to nitrogen. The results are expressed as ppm metolachlor.

For CGA-49751, the initial sample hydrolysis with dilute hydrochloric acid is as above. The acid extract is partitioned with dichloromethane which separates CGA-49751 and CGA-37913. The dichloromethane phase containing CGA-49751 is washed with a dilute sodium carbonate solution, and converted to the chloroethanol derivative by reaction with boron trichloride/2-chloroethanol. The derivative is extracted into hexane, and an aliquot of the extract is cleaned up on a silica gel column followed by a alumina column. The eluate is concentrated, and the CGA-49751 is determined as above. The results are expressed as ppm metolachlor.

We have concluded (PP#8F2081) that the methods are adequate for enforcement of corn tolerances.

Enforcement methods are available (PAM II) for atrazine, cyanazine (Bladex), dicamba, glyphosate, paraquat, and simazine.

Adequate analytical methods are available for enforcement purposes.

Residue Data

No new residue data are submitted for corn. The petitioner has included previously submitted corn residue data by reference to earlier petitions (PP#5F1606, 8F2081). We have previously reviewed these data and concluded that residues of metolachlor were not likely to exceed levels of 0.1 ppm for fresh corn including sweet corn (kernels plus cobs, husks removed); 0.1 ppm for popcorn grain; and 1 ppm for corn forage and fodder.

The residue levels resulted from maximum proposed (3.0 lb act/A) and exaggerated (2X) application rates.

The maximum proposed application rate above (3.0 lb act/A) is the same maximum rate proposed in this petition. Additionally, the tank-mix uses in this petition permit a post emergence application of metolachlor at a maximum of 3.0 lb act/A when corn is no more than 5 inches tall.

In view of the foregoing, we conclude that residues of metolachlor (applied alone or in tank-mixtures) in or on fresh corn including sweet corn (kernels plus cobs, husks removed) and popcorn grain are not likely to exceed the proposed tolerance level of 0.1 ppm.

The established corn forage and fodder tolerance is adequate to cover residues resulting from the proposed and registered uses.

Tank-mix uses

No residue data are submitted for metolachlor when used in tank-mixtures with the various herbicides (atrazine, cyanazine, dicamba, glyphosate, paraquat, simazine). Residue data were submitted in PP#8F2081 for tank-mixtures of metolachlor and atrazine applied to corn. The data showed that the level of metolachlor residues were not affected by the presence of atrazine. (The chemical atrazine, cyanazine, and simazine all belong to the same s-triazine class.)

We do not expect the residue levels of metolachlor or the various compounds proposed for tank-mix uses to be affected by the tank-mix uses.

Additionally, since the proposed rates for atrazine, cyanazine, dicamba, glyphosate, paraquat and simazine are within the registered rates, we do not expect residues of these compounds to exceed the established tolerances in corn.

Meat, Milk, and Eggs

We have concluded in PP#8F2081 that the feed uses of corn grain and corn forage and fodder could result in eggs, milk, and meat of livestock [§180.6(a)(2)]. We reiterate this conclusion. However, we believe that the established tolerance of 0.02 ppm for eggs, milk, and meat of livestock (§180.368) is sufficient to cover such residues.

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Metolachlor

PETITION NO. 1F2521

CCPR NO. ---

Codex Status☒ No Codex Proposal
Step 6 or above

Residue (if Step 9): _____

<u>Crop(s)</u>	<u>Limit (mg/kg)</u>
NONE	

CANADIAN LIMITResidue: presumably
parent compound

<u>Crop</u>	<u>Limit (ppm)</u>
Corn	0.1*

Proposed U.S. Tolerances2-chloro-N-(2-ethyl-6-methylphenyl)-
N-(2-methoxy-1-methylethyl)acetamide
and its metabolites 2-[(2-ethyl-6-
methylphenyl)amino]-1-propanol and
4-(2-ethyl-6-methylphenyl)-2-hydroxy-
Residue: 5-methyl-3-morpholinone

<u>Crop(s)</u>	<u>Tol. (ppm)</u>
Fresh corn including sweet corn (kernels plus cobs, husks removed)	0.1 ppm
Popcorn Grain	0.1 ppm

MEXICAN TOLERANCIA

Residue: _____

<u>Crop</u>	<u>Tolerancia (ppm)</u>
NONE	

Notes: * Negligible residue type limit