US EPA ARCHIVE DOCUMENT

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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SUBJECT: PP#1F2495: Metolachlor in Seed and Pod Vegetables. Evaluation of analytical method and residue data.

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The CIBA-GEIGY Corp., proposes a tolerance 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 in or on seed and pod vegetables (dry or succulent) at 0.3 ppm.

Seed and pod vegetables (dry or succulent) include black-eyed peas, cowpeas, dill, edible soybeans, field beans, field peas, garden peas, green beans, kidney beans, lima beans, navy beans, okra, peas, pole beans, snap beans, string beans, wax beans, other beans and peas, and lentils [§180.34(f)].

Permanent tolerances are established for metolachlor 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 ppm (PP#9F2213); sorghum grain at 0.3 ppm and sorghum forage and fodder at 2.0 ppm (§180.368).

Tolerances are pending for metolachlor residues in sunflower seed at 0.3 ppm (PP#0E2416), flax at 0.2 ppm (PP#0E2417), and cottonseed at 0.1 ppm (PP#1F2506).

Conclusions

1. The nature of the residue 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 in seed or pod vegetables are not likely to exceed the proposed tolerance

3b. Residues of eptam or dinoseb in or on beans are not likely to exceed the established tolerances due to the tank-mix uses or uses following metolachlor treatments.

3c. The label restriction against the grazing or feeding of forage and fodder precludes the need for tolerances on these items at this time.

4. Residues of metolachlor could occur in eggs, milk, and meat of livestock due to the proposed uses [§180.6(a)(2)]. However, such residues would be adequately covered by the established tolerances.

Recommendation

TOX and EFB considerations permitting, we recommend for the proposed tolerances.

If the petitioner anticipates removal of the grazing and forage and hay feed restrictions, then additional livestock feeding studies at levels higher than those now available may be needed.

DETAILED CONSIDERATIONS

Proposed Uses

Metolachlor, formulated as Dual 8E (8 lb act/gal), is proposed for preplant or premergence application for grass and weed control in seed and pod vegetables.

Pod Crops [including garbanzo, great northern beans, guar, kidney beans, lima beans, mung beans, navy beans, okra, peas (English; southern peas, such as blackeye, pinkeye, crowder, etc.), pinto beans, and snap beans (green, wax, string)]: apply metolachlor alone as a preplant incorporated or preemergence application at rates of 1.5-3.0 lb act/A depending upon the soil texture.

Metolachlor and eptam are to be applied as a tank-mix to beans (green and dry) preplant incorporated at rates of 1.25-2.5 lb metolachlor/A plus 3-4 lb eptam/A. Both chemicals may be applied sequentially with eptam alone as indicated on its label followed by metolachlor alone as indicated above (1.25-2.5 lb act/A).

Metolachlor and Premerge are to be applied as a tank-mix to beans (field, lima, and snap) preemergence or just before or during early emergence when beans are in, but not beyond, the crook stage at rates of 1.25-2.5 lb metolachlor/A plus 3-4.5 lb premerge/A. Compounds may be applied sequentially with 1.25-2.5 lb metolachlor/A followed by 3-4 lb premerge/A.

Eptam, (S-ethyl dipropylthiocarbamate), has an established tolerance of 0.1 ppm on beans (green and dry). Eptam is registered for preplant use on beans at 4.0 lb act/A and post emergence use at layby at 3.0 and 4.0 lb act/A. Eptam is not to be used preplant on cowpeas, lima beans, soybeans, or other flat pod beans except Romano.

Premerge (dinoseb), 2-sec-butyl-4,6-dinitrophenol, alkanolamine salts of the ethanol and isopropanol series, is registered for use on beans at 1.25-9.0 lb act/A (preplant, preemergence, emergence, and post emergence (also as indicated above for emergence). Dinoseb has an established tolerance of 0.1 ppm for beans, forage, and hay.

There are restrictions on the grazing or feeding of forage or fodder from pod crops treated with metolachlor or the tank-mixes with eptam or dinoseb.

The formulations' inert ingredients are cleared for use under §180.1001. The manufacturing process and the composition of technical metolchlor 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 form those in plants, the metabolic componets 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 reluxed 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 an alumina column. The eluate is concentrated, and the CGA-49751 is determined as above. The results are expressed as ppm metolachlor.

Untreated (control) samples of bean seed, pods, and forage had <0.03-0.09 ppm metolachlor-equivalent residues. The 0.09 ppm value was for forage. Control samples of beans, pods and forage were fortified with the metabolites CGA-37913 and CGA-47951 at levels of 0.02-1.0 ppm. Recoveries were 46-124%.

The methods have been successfully tested with metolchlor and its metabolites on corn grain and meat. We believe the results of the method trials can be extended to include beans and bean forage.

Adequate analytical methods are available for enforcement purposes for metolachlor residues.

Eptam (S-ethyl dipropylthiocarbamate)

A sample is extracted by blending with benzene and filtering. The extract is cleaned up on an alumina column, and eptam is eluted with a benzene/acetone mixture. The eluate is concentrated, and eptam is determined by gas chromatography using a nitrogen-sensitive detector. The detection limit is reported to be 0.02 ppm.

Control samples of beans, pods, and forage had <0.02-0.10 ppm eptam-equivalent residues. Control samples, fortified with eptam at levels of 0.05 ppm and 0.1 ppm, yielded recoveries of 76-128%.

The method appears to be adequate for the determination of eptam residues in beans, peas, and their forages.

A regulatory method for eptam is available (PAM II, S-ethyl dipropylthiocarbamate). The residues are steam distilled from the crop and determined by gas chromatography using the microcoulometric detection system (MCGC).

Dinoseb (2-sec-butyl-4,6-dinitrophenol)

A sample is extracted with a solvent mixture of methanol/sulfuric acid followed by partitioning into diethyl ether. The ether phase is cleaned up on an alumina column, and dinoseb is eluted with sodium bicarbonate. The eluate is acidified, and dinoseb is partitioned into ether. The ether phase is treated with diazomethane to form the methyl ether derivative of dinoseb. The ether is removed, and the residues are cleaned up on an alumina column and determined by gas chromatography using an electron capture detector.

Control samples of beans, pods, and forage had no detectable residues (<0.05 ppm) of dinoseb. control samples were fortified with dinoseb at levels of 0.05-1.0 ppm. Recoveries were 74-100%.

This method has been validated by Yip and Howard of FDA [JAOAC 51, 24(1968)] to 0.2 ppm. The method's sensitivity is better than 0.05 ppm.

Adequate analytical methods are available for enforcement purposes.

Residue Data

Samples of beans, pods, forage, and peas were obtained from crops in New York, California, Pennsylvania, and Wisconsin which had been treated as proposed at rates of 3 lb act/A and 6 lb act/A (2X maximum proposed rate).

The green beans or dry beans had no detectable (<0.05 ppm) metolachlor residues at 88-163 days after treatment (PHI) from the 1X or 2X rates. The green pods had residues of 0.10-0.53 ppm at 88-117 days from the 1X rate. From the 2X rate, residues in green pods were 0.15-0.93 ppm at 88-92 days and 0.45-0.67 ppm at 117-123 days. the dry pods had residues of 0.14-0.45 ppm at 158 days from the 1X rate and 0.64-0.99 ppm at 158 days from the 2X rate. The combined green beans plus pods had residues of <0.05-<0.14 ppm at intervals of 58-123 days after treatment due to the 1X rate. At the 2X rate, residues in green beans and pods were <0.13-0.25 ppm at 58 days and <0.05 ppm at 123 days.

The bean forage had residues of <0.05-10.2 ppm at 45-63 days due to the 1X rate. At the 2X rate, residues were 1.6-21.7 ppm at 45-53 days and <0.05-0.50 ppm at 59-63 days.

Residues in beans or peas (dry or succulent) are not likely to exceed the proposed tolerance (0.3 ppm) from the proposed use.

Residue in the forage could be as high as 10 ppm when the crops are ready to pasture (e.g., cowpeas are ready for pasture at 45-60 days after treatment.) No tolerance is proposed for the forages. However, the feeding restrictions on the label alleviate our concern over the feed use of these items.

Tank-Mixtures

Metolachlor & eptam - samples which had been treated at rates of 2.5 lb metolachlor plus 4.0 lb eptam (maximum proposed rates) were collected at intervals of 45-189 days and analyzed for residues.

Metolachlor residues were <0.05 ppm (method sensitivity) and eptam residues were 0.02 ppm in dry beans at 95 days after treatment (PHI). The dry pods had 0.17-0.39 ppm metolachlor residues and <0.05 ppm eptam residues at 117 days. The beans and pods had <0.05-0.22 ppm metolachlor residues at 58-123 days and <0.02 ppm eptam residues. The forage had 1.7-3.6 ppm metolachlor and <0.02 ppm eptam at 45-53 days. At 63 days the forage had <0.05-<0.12 ppm metolachlor residues and <0.02-0.045 ppm eptam residues.

Metolachlor residues in beans are not likely to exceed the proposed tolerance (0.3 ppm) from the tank-mix use or the sequential use. However, as concluded with metolachlor used alone, residues of metolachlor will occur in the forage when ready to pasture. A tolerance is needed to cover such residues.

Eptam residues in beans and the forage are not likely to exceed the established tolerance (0.1 ppm) for beans (green and dry).

Metolachlor & dinoseb - samples which had been treated at 2.5 lb metolachlor plus 4.5 lb dinoseb (maximum proposed rates) were collected at intervals of 45-189 days and analyzed for residues. Metolachlor residues were <0.05 ppm in dry beans and <0.05-0.11 ppm in green beans at 45-189 days. the dry pods had <0.16-0.34 ppm metolachlor residues at 117-163 days and <0.05 ppm at 189 days. The green pods had <0.05-0.31 ppm metolachlor residues at 72-117 days. The green forage had metolachlor reisdues of <0.05-8.5 ppm at 45-63 days.

No residues of dinoseb were detected (<0.05 ppm) in green or dry beans, green or dry pods, beans and pods, or bean forage at 45-189 days.

Metolachlor residues in beans are not likely to exceed the proposed tolerance (0.3 ppm) from the tank-mix use or the sequential use. However, residues of metolachlor will occur in the forage when ready to pasture.

Dinoseb residues in beans and the forage are not likely to exceed the established tolerance (0.1 ppm) for beans, forage and hay.

Forage and hay

No tolerance is proposed for the forage, hay, and straw of seed and pod vegetables (succulent or dry). The residue data show that levels of 10.2 ppm could occur in the forages when ready to pasture (as early as 45 days after treatment). No data are submitted for hays or straws. However, a single tolerance level of 15 ppm would be adequate to cover residues in the forage, hay, and straw. (Crops would be harvested for hay at intervals of 120 days or more after treatment.) The residue data indicate that residues generally would be lower at longer PHI's. However, the need for tolerances at this time is resolved by the grazing/feeding restrictions for forage and fodder.

Meat, Milk, and Eggs

Beans, bean vines, bean straw, bean cannery residue, peas, pea vines, and pea straw may be used as livestock feeds. By using the proposed tolerance for beans and peas (0.3 ppm) and the percentages of the various items in the livestock diets, we can estimate the maximum levels of metolachlor residues likely to be ingested.

The ingestion levels are: cattle (0.06 ppm); poultry (0.05 ppm); hogs (0.03 ppm); horses (0.03 ppm); goats and sheep (0.06 ppm). (The restrictions on the grazing and feed use of forages and hays preclude the ingestion of residues from these sources.)

Permanent metolachlor tolerances are established at 0.02 ppm in eggs, milk, meat, fat, and meat byproducts of livestock. The tolerances are supported by livestock feeding studies in which dairy cows and goats were feed metolachlor residues at levels of 0-5 ppm and laying hens were fed at levels of 0-2 ppm (PP#'s 7F1913, 9F2203, 9F2213). In view of the maximum ingestion levels indicated above, we conclude that any metolachlor residues which might occur in eggs, meat, or milk due to the feed use of seed and pod vegetables and their forages, hays, and straw would be adequately covered by the established tolerances [§180.6(a)(2)].

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Metolachlor

PETITION NO. 1F2495

CCPR NO. NONE

Codex Status

/X/ No codex Proposal Step 6 or above

Residue (if Step 9): _____

Crop(s)	Limit (mg/kg)
NONE	

Proposed U.S. Tolerances

2-Chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide and its metabolites 2-[(2-ethyl-6-methylphenyl)amino]-1-propanol and

Residue: 4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholinone

Crop(s)	Tol. (ppm)
Seed and Pod Vegetables (dry and succulent)	0.3 ppm

CANADIAN LIMIT

Residue: parent (as far as we know)

Crop	Limit (ppm)
Soybeans	0.1 (negligible residue)

MEXICAN TOLERANCIA

Residue: _____

Crop	Tolerancia (ppm)
NONE	

NOTES: