

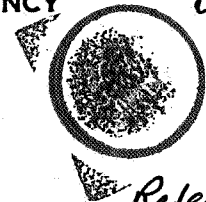
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Atrazine / Review # 49 / 11 pages / 1.5.83

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

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JAN 5 1983

Releasable

MEMORANDUM

SUBJECT: PP3F2772/FAP3H5371 Atrazine on Sugarcane
Evaluation of analytical method and residue data

FROM: R. W. Cook, Chemist *RLW Cook*
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THRU: Charles L. Trichilo, Chief
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TO: Robert Taylor, PM 25
Registration Division (TS-767)
and
Toxicology Branch
Hazard Evaluation Division (TS-769)

The petitioner, Ciba-Geigy Corporation, proposes establishment of a tolerance for residues of the herbicide atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and its chlorometabolites: 2-amino-4-chloro-6-ethylamino-s-triazine (hereinafter called by company code name G-28279); 2-amino-4-chloro-6-isopropylaminos-triazine (G-30033); and 2-chloro-4,6-diamino-s-triazine (G-28273) in or on the raw agricultural commodity sugarcane at 0.25 ppm. In addition, the petitioner proposes feed additive tolerances for atrazine and its chlorometabolites G-28279, G-30033, and G-28273 in sugarcane bagasse at 0.5 ppm and in molasses at 1.5 ppm.

Tolerances are established in §180.220(a) for residues of the herbicide atrazine per se in a number of commodities, including sugarcane, sugarcane fodder, and sugarcane forage at 0.25 ppm. Additionally, in §180.220(b) tolerances for combined residues of atrazine and its metabolites G-28279, G-30033, and G-28273 are established for range grass. Therefore, one net effect of the current petition is to shift the raw

agricultural commodity from §180.220(a) to §180.220(b), to include the specific metabolites under the tolerance expression.

In addition, the petitioner requests amended uses for tank mixtures of atrazine & diuron, and atrazine & ametryn on sugarcane. The amended registration request for tank mixes on sugarcane has been reviewed previously (L.M. Bradley, 11/20/80, amended use files for 100-439, -497, -535, and -585 and 100-473).

Tolerances for ametryn on sugarcane, and sugarcane forage and fodder are established (40 CFR 180.258) at 0.25 ppm. A tolerance for diuron on sugarcane at 1 ppm is established (40 CFR 180.106).

The proposed uses are specifically limited to Florida, Hawaii, and Texas.

Conclusions

1. The metabolism of atrazine in plants and animals is adequately understood. The residue of concern is atrazine and its metabolites G-28279, G-30033, and G-28273.
2. Adequate analytical methods are available for enforcement purposes.
3. Combined residues of atrazine and its metabolites G-28279, G-30033, and G-28273 in or on the raw agricultural commodity sugarcane are not likely to exceed the proposed 0.25 ppm tolerance.
- 4a. The proposed feed additive tolerances of 0.5 ppm for sugarcane bagasse and 1.5 ppm for sugarcane molasses are adequate to cover expected combined residues of atrazine and its metabolites G-28279, G-30033, and G-28273 resulting from the proposed use.
- 4b. The proposed food additive tolerance of 1.5 ppm for sugarcane molasses is adequate to cover expected combined residues of atrazine and its metabolites G-28279, G-30033, and G-28273.
5. The established meat, milk, poultry and egg tolerances are not likely to be exceeded from ingestion of animal feeds containing residues resulting from the proposed use.
- 6a. Residues of ametryn in or on the raw agricultural commodities sugarcane and its forage and fodder resulting from the proposed tank mix use are not likely to exceed the existing 0.25 ppm tolerance.

6b. Residues of diuron in or on raw agricultural commodity sugarcane resulting from the proposed tank mix use are not likely to exceed the existing 1 ppm tolerance.

7. Section F should be revised substituting the word "metabolites" for the word "chlorometabolites," to be consistent with the current 40 CFR 180.220(b).

8. A revised Section F is needed, proposing appropriate tolerances for combined residues of atrazine and its metabolites G-28279, G-30033, and G-28273 in or on the raw agricultural commodities sugarcane forage and sugarcane fodder. A tolerance level of 1 ppm for sugarcane forage and fodder is appropriate. Alternately, a revised Section B is needed, proposing a practical livestock grazing and feeding restriction; and further, a request for revocation of the currently existing tolerances (0.25 ppm) for atrazine per se in or on sugarcane forage and fodder is needed.

9. There are no Codex, Mexican or Canadian tolerances for atrazine on sugarcane (See attached codex sheet).

Recommendations:

We recommend against establishment of the proposed tolerances for the reasons cited in conclusions 7 and 8.

DETAILED CONSIDERATIONS

Formulations:

Four formulations of atrazine are proposed for use on sugarcane: AAtrex® 4L and AAtrex® 4LC (both 4 lb/gal EC), AAtrex® 80W (a 76% wettable powder) and AAtrex® Nine-0 (an 85.5% water-dispersible granular formulation). Information from PM team 25 indicates that the inerts in these formulations are cleared. (Telecon, 12/3/82, J. Dzuiban-R.W. Cook).

Directions for Use:

Atrazine is to be applied alone or in tank mix combinations with ametryn or diuron. Application may be aerial or ground. Repeat applications as described below may be made with final application prior to "close-in." Do not exceed the rate of herbicide suggested for any one crop of sugarcane. Weeds should be treated <1.5 inches in height. Directions are specific to each state.

Florida: For plant or ratoon crop: Apply 4 lbs ai/A preemergence and one or two post emergence applications to sugarcane and weeds at 2 lb ai/A.

or

Apply 1-3 times as needed at 2 lb ai/A postemergence to sugarcane and weeds. For control of emerged pellitory weed apply 0.4 - 0.6 lb ai/A prior to "close-in."

Hawaii: For plant or ratoon crop: Apply tank mixture of 2-4 lb ai/A atrazine plus 2-4 lb ai/A diuron preemergence to sugarcane and weeds either after planting or after harvesting plant crop for ratoon crop. A second application at the above rates may be made after sugarcane and weeds emerge. Third application at 2-2.4 lb ai atrazine & 2-2.4 lb ai diuron per acre may be made,

or

Apply tank mixture of 2-4 lb ai atrazine & 4-8 lb ai ametryn preemergence. Second application postemergence at 2-4 lb ai atrazine & 2-4 lb ai ametryn may be made. Third application at 2-2.4 lb ai atrazine & 2-4 lb ai ametryn may be made prior to "close-in."

Texas: For plant or ratoon crop: Apply 4 lb ai/A atrazine preemergence. Two additional applications at 3 lb ai/A postemergence may be made.

or

Apply 2-4 lb ai atrazine & 1.2-2 lb ai ametryn interline or over-the-top of plant or ratoon sugarcane, before or after emergence. Follow with one or two repeat applications as needed. Do not apply more than 10 lb ai/A of atrazine to any one crop of sugarcane.

Use of unspecified nonionic surfactant is recommended for several of the above use patterns.

Ametryn is currently registered at 4-8 lb active/A at planting or after ratooning, plus up to two interline applications of 2-4 lb active/A. No more than 16 lb ai/crop may be applied, and no applications are to be made after "close-in."

Diuron is registered at up to 6.4 lb ai/A (3.0 in FL and LA) after planting or harvesting, with two additional applications made between rows using 3.2 lb ai/A (1.6 lb in FL and LA). No more than 9.6 lb ai/A may be used per crop cycle (4.8 lb in FL and LA).

Direction for Use:

Atrazine is to be applied alone or in tank mix combinations with ametryn or diuron. Application may be aerial or ground.

Repeat applications as described below may be made with final application prior to "close-in." Do not exceed the rate of herbicide suggested for any one crop of sugarcane. Weeds should be treated < 1.5 inches in height.

Directions are specific to each state.

Florida: For plant or ratoon crop: Apply for lbs ai/A preemergence and one or two postemergence applications to sugarcane and weeds at 2 lb ai/A.

or

Apply 1-4 times as needed at 2 lb ai/A postemergence to sugarcane and weeds. For control of emerged pellitory weed apply 0.4 - 0.6 lb ai/A prior to "close-in."

Hawaii: For plant or ratoon crop: Apply tank mixture of 2-4 lb. ai/A atrazine plus 2-4 lb ai/A diuron preemergence to sugarcane and weeds either after planting or after harvesting plant crop for ratoon crop. A second application at the above rates may be made after sugarcane and weeds emerge. Third application at 2-2.4 lb ai atrazine + 2-2.4 lb ai diuron per acre may be made.

or

Apply tank mixture of 2-4 lb ai atrazine + 4.8 lb ai ametryn preemergence. Second application post-emergence at 2-4 lb ai atrazine + 2-4 lb ai ametryn may be made. Third application at 2-2.4 lb ai atrazine + 2-4 lb ai ametryn may be made prior to "close-in."

Texas: For plant or ratoon crop: Apply 4 lb ai/A atrazine preemergence. Two additional applications at 3 lb ai/A post emergence may be made.

or

Apply 2-4 lb ai atrazine + 1.2-2 lb ai ametryn interline or over-the-top of plant or ratoon sugarcane, before or after emergence. Follow with one or two repeat applications as needed. Do not apply more than 10 lb ai/A of atrazine to any one crop of sugarcane.

Use of unspecified nonionic surfactant is recommended for several of the above use patterns.

Ametryn is currently registered at 4-8 lb active/A at planting or after ratooning, plus up to two interline applications of 2-4 lb active/A. No more than 16 lb ai/crop

Diuron is registered at up to 6.4 ai/A (3.0 in FL and LA) after planting or harvesting, with two additional applications made between rows using 3.2 lb ai/A (1.6 lb in FL and LA). No more than 9.6 lb ai/A may be used per crop cycle (4.8 lb in FL and LA).

Nature of the Residue

No new metabolism data for atrazine is submitted. However, the metabolism of atrazine in both plants and animals is well understood. Atrazine is metabolized in both plants and animals by conjugate formation, hydroxylation, and N-dealkylation. Depending on plant species and stage of growth, the predominant metabolic pathway may be conjugate formation, and/or hydroxylation, and/or N-dealkylation. Conjugation with glutathione and [γ]-glutamylcysteine occurs in many monocotyledonous plants as does formation of hydroxy atrazine. Formation of both deethylated and deisopropylated atrazine has been noted. Dealkylation may either precede or follow formation of hydroxy atrazine. (PP4F1425, D.V. Reed, 2/7/74). We conclude the metabolism of atrazine is adequately understood. The residue of concern is atrazine per se and its chlorometabolites G-28279, G-30033, and G-28273.

Analytical Methods:

The analytical method AG-295 used for determining atrazine and two metabolites G-30033 and G-28279 was also used to determine ametryn and two of its metabolites 2-amino-4-(isopropylamino)-6-(methylthio)-s-triazine (GS-11354) and 2-amino-4(ethylamino)-6-(methylthio)-s-triazine (GS-11355). In brief, residues are extracted with 10% water: acetonitrile and partitioned into dichloromethane or extracted with chloroform, depending on water content of sugarcane. The extract is taken to dryness, dissolved in carbon tetrachloride, cleaned-up on alumina and eluted with ethylether in dichloromethane. After transfer to toluene, the residues are quantitated by GC-EC in nitrogen-specific mode and the method sensitivity is reported as 0.05 ppm.

Recovery values at 0.05 ppm fortification levels were 80-118% for atrazine, 91-126% for G-30033, and 80-126% for G-28279, while for ametryn, recoveries were 77-123%, 73-110% for GS-11354, and 72-108% for GS-11355.

The atrazine metabolite G-28273 and the ametryn metabolite GS-26831 are determined by method AG-281. In brief, these residues are extracted with methanol, washed with hexane, evaporated to dryness, partitioned by liquid-liquid chromatography, eluted from alumina column with ethyl ether. The method sensitivity is 0.1 ppm when determined by EC-GC in the nitrogen-specific mode. Reported recoveries at 0.1 ppm

The method sensitivity is 0.1 ppm when determined by EC-GC in the nitrogen-specific mode. Reported recoveries at 0.1 ppm fortification level were 80-113% for G-28273 and 85-110% for GS-26831.

The method of Baunok and Geissbuehler (1968) (Bull. Env. Contam. and Tox.) was used to determine diuron, at a reported method sensitivity of 0.05 ppm. Reported recoveries for sugarcane at fortification levels of 0.1, 0.5, and 1.0 ppm were 105-118%.

A successful method tryout on potatoes was conducted on a method similar to AG-295 in conjunction with PP638 (ametryn) and PP620 (atrazine). MTO recovery values for atrazine were 76-94% at 0.25-0.5 ppm fortification levels. We consider the analytical method adequate for enforcement purposes.

Residue Data:

1. Three studies from Hawaii reflecting residue levels from the atrazine plus diuron tank mix (3 applications at 1X rate, 2 studies ground equipment, one study aerial equipment) are submitted. Residues in whole sugarcane at 258-312 days PHI were <0.05 ppm for diuron, atrazine, G-30033 and G-28279, and <0.1 ppm for G-28273. (Test No. 5398, 5401, 5402).

Residue levels of atrazine and its metabolites are not likely to exceed the proposed tolerance in sugarcane from the proposed tank mix of diuron and atrazine. Residue levels of diuron are not likely to exceed the existing tolerance of 1 ppm in or on sugarcane.

2. Residue data from six studies (2 in Hawaii, both 3 applications at 1X rate by ground equipment, and 4 in Texas, 3 studies by three ground applications at 1X rate and 1 study of three aerial applications at 1X rate) are submitted reflecting tank mix application of atrazine and ametryn. Although dosage rates differ between the two states, applications do reflect maximum permitted dose in each state. In Hawaii, residue levels in sugarcane were <0.05 ppm for ametryn, GS-11354, GS-11355, atrazine, G-30033, and G-28279, and <0.1 ppm of GS-26831 and G-28273. In the Texas tank mix studies, one sample of stripped sugarcane at 107 days PHI showed 0.07 ppm of the atrazine metabolite G-30033, while residue levels in the remainder of the samples were not detectable, at the levels mentioned for Hawaii, above. (Test No. 5399, 5397, 4452, 4540, 4453, 4539). We do not expect residue levels of atrazine and its metabolites to exceed the proposed 0.25 ppm tolerance in or on sugarcane from the proposed tank mix with ametryn. Further, we do not expect residue levels of ametryn to exceed the existing 0.25 ppm tolerance in or on sugarcane and its forage and fodder from the proposed tank mix of atrazine and ametryn.

3. In addition to the above discussed tank mixes, the use directions recommend application of atrazine alone. Nine studies in FL(5) and TX(4) are submitted reflecting maximum recommended rates in those states. In FL, three studies reflect the recommended 3 postemergence applications at 2 lb ai/A, and two studies reflect the recommended 4 lb ai/A preemergence plus 2 postemergence applications at 2 lb ai/A. Four TX studies reflect the recommended 4 lb ai/A preemergence plus two 3 lb ai/A postemergence applications. Two studies employing aerial application are included in the nine trials. (Test No. 3870, 4442, 3867, 3868, 4452, 4453, 4539, 4540). Residue levels in these nine studies, except one sample, were all <0.05 ppm for atrazine, G-30033, and G-28279, and <0.1 ppm for G-28273 in whole cane (FL) or stripped cane (TX) at 138 to 209 days PHI. The one exception in TX showed 0.09 ppm of G-30033 in stripped cane at 140 days PHI, while atrazine, G-28279, and G-28273 were all non-detectable at the above cited levels.

Other studies in FL, TX, or LA at below or up to 2.4X recommended rates are submitted. Only two samples showed atrazine at 0.04-0.05 ppm level, while one sample showed combined 0.05 ppm of G-30033 plus G-28279. Both samples reflect exaggerated dosages.

We conclude that residue levels of combined atrazine and its metabolites are not likely to exceed the proposed 0.25 ppm tolerance in or on sugarcane.

Sugarcane Forage and Fodder

No residue data are available for forage and fodder per se. However, in seven trials, residue data are available for sugarcane leaves, which would constitute part of the forage or fodder available from sugarcane. Combined residues on sugarcane leaves ranged from non-detectable to about 0.9 ppm (0.71 ppm G-28273 & 0.15 ppm G-30033). Therefore, a tolerance level of 1 ppm for combined residues of atrazine and its metabolites in sugarcane forage and fodder appears appropriate.

Sugarcane Byproducts

We have previously reviewed four sugarcane processing studies and have concluded (L.M. Bradley, 11/20/80):

1. Residues of atrazine and its three metabolites G-28279, G-30033 and G-28273, if any, in recrystallized sugar are <0.02 ppm.

concentration of residues in bagasse and molasses, feed additive tolerances for these two byproducts are necessary. Appropriate feed additive tolerances would be 0.5 ppm for sugarcane bagasse and 1.5 ppm for sugarcane molasses.

The petitioner has proposed feed additive tolerances for bagasse and molasses at 0.5 and 1.5 ppm, respectively. We conclude that combined residues of atrazine and its three metabolites are not likely to exceed the proposed feed additive tolerance of 0.5 ppm in sugarcane bagasse or 1.5 ppm in sugarcane molasses. Further, the petitioner has proposed a food additive tolerance of 1.5 ppm for combined residues of atrazine and its three metabolites G-28273, G-30033, and G-28279 in sugarcane molasses. We conclude that combined residues of atrazine and its metabolites are not likely to exceed the proposed tolerance of 1.5 ppm in sugarcane molasses.

Meat, Milk, Poultry and Eggs:

In our previous review (L.M. Bradley, 11/20/80), we concluded that the existing 0.02 ppm tolerance for atrazine in meat and milk is adequate to cover the relatively minor contributions of bagasse (very minor feed item for cattle) and molasses (1.5 ppm at <20% of diet = 0.3 ppm in diet).

The sugarcane byproduct residue contribution is minor compared to the ingestion of range grass (70% of diet at 4 ppm) or corn fodder containing 15 ppm. We reiterate herein that existing meat and milk tolerances are not likely to be exceeded by the ingestion of residues from processed sugarcane commodities. Further, sugarcane molasses may be fed to laying hens at <4% of the diet, yielding 0.06 ppm in the diet. Since established poultry and egg tolerances cover higher residue ingestion levels, we reiterate herein that existing poultry and egg tolerances are not likely to be exceeded.

While sugarcane forage is reported to constitute 20% of the diet of beef cattle and up to 40% for dairy cattle, the contribution from sugarcane forage bearing 1 ppm is minor compared to corn fodder at 15 ppm or range grass at 4 ppm. Other information in our files (see T. Woodward memos of 1/5/72 and 1/20/72 in Sugarcane Cultural Practices File) indicates that most sugarcane leaves are burned off and very insignificant amounts of sugarcane forage and fodder are ever consumed by livestock. A labeling restriction prohibiting such livestock feeding would be practical.

OTHER CONSIDERATIONS

An International Residue Limit Status sheet is attached.

R. W. Cook

INTERNATIONAL RESIDUE LIMIT S. US

CHEMICAL Atrazine

PETITION NO 3F 2972 / 3H 5371

CCPR NO. _____

Codex Status

Proposed U. S. Tolerances

No Codex Proposal
Step 6 or above

*Atrazine and its metabolites**

Residue (if Step 9): _____

Residue: _____

Crop(s) Limit (mg/kg)

Crop(s) Tol. (ppm)

Sugarcane	0.25
Bagasse	0.50
Molasses	1.50

CANADIAN LIMIT

MEXICAN TOLERANCIA

Residue: _____

Residue: _____

Crop Limit (ppm)

Crop Tolerancia (ppm)

None on sugarcane

None on sugarcane

* 2-amino-4-chloro-6-ethylamino-s-triazine ;
 2-amino-4-chloro-6-isopropylamino-s-triazine
 2-chloro-4,6-diamino-s-triazine

Notes: