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EEB

WASHINGTON, D.C. 20460

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MEMORANDUM

SUBJECT: PP#1F2540. Terbufos in Sorghum.
Evaluation of analytical method and residue data.

FROM: Alfred Smith
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THRU: Charles L. Trichilo, Chief
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TO: William Miller, Product Manager No. 16
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Registration Division (TS-767)
and
Toxicology Branch
Hazard Evaluation Division (TS-769)

The American Cyanamid Company proposes tolerances for residues of the insecticide terbufos, (S-[[(1,1-dimethylethyl) thio] methyl] O,O-diethyl phosphorodithioate; Counter), and its cholinesterase-inhibiting metabolites in or on sorghum grain at 0.05 ppm and sorghum forage and fodder at 0.5 ppm.

Tolerances for terbufos are established (§180.352) on sugarbeet roots (0.05 ppm), sugarbeet tops (0.1 ppm), corn grain (0.05 ppm), and corn forage and fodder (0.5 ppm).

A tolerance of 0.2 ppm for cabbage, broccoli, and cauliflower is pending (PP#1F2433).

Conclusions

1. The nature of the residue is adequately understood. The parent compound terbufos and its cholinesterase inhibiting metabolites are the significant components of the residues in plants and animals.

2. An adequate analytical method is available for enforcement purposes.

3a. Residues in or on sorghum grain, grain fractions, or sorghum forage are not likely to exceed the proposed tolerances. No detectable residues were reported in sorghum grain.

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3b. No residue data are submitted for sweet sorghum. The use is apparently intended for grain sorghum only. If this is the case, the petitioner should clarify Section B to indicate that the use is for grain sorghum. If use on sweet sorghum is intended, residue data for this commodity, as well as for sorghum syrup will be needed.

4. No residues are likely to occur in eggs, milk, meat, fat, and meat byproducts of cattle, goats, hogs, horses, poultry, and sheep [§180.6(a)(3)].

Recommendation

Contingent upon the resolution of conclusion 3(b) above and TOX and EFB considerations, we recommend for the proposed tolerances.

DETAILED CONSIDERATIONS

Proposed Use

Terbufos is formulated as Counter® 15G, a granulated solid containing 15% a.i., to be used for the control of greenbugs in sorghum.

Terbufos is to be applied at planting as a band at rates of 1.2-2.4 oz act. per 1,000 ft. of row (minimum 20-inch row spacing).

The use appears to be intended for grain sorghum. The petitioner should clarify this intent in Section B. If use is intended for sweet sorghum, residue data will be needed for this commodity as well as for sorghum syrup.

The formulations inert ingredients are cleared for use under §180.1001.

Technical grade terbufos is discussed in PP#4F1496. The impurities are not likely to create a residue problem.

Nature of the Residue

Sorghum plants were grown in soil which was treated with radiolabelled C^{14}-terbufos (CL 92,100) at a rate equivalent to 1.0 lb/A.

Samples of plants were collected at 1 and 2 months and at harvest (4 months after treatment). The samples of plants and grain were examined for radioactivity.

The study shows that terbufos is absorbed from the soil by sorghum plants, translocated, and metabolized. Plant and grain residues consist of the parent compound terbufos, it cholinesterase-inhibiting metabolites, and reincorporated C^{14}-activity. (See the accompanying chart for chemical and structural identification of residue components.)

The modes of metabolism and/or degradation consist primarily of oxidation of the sulfur atoms, dealkylation, and hydrolysis.

Analysis of the samples consisted of extraction and partitioning with organic solvents. Aliquots of the various solvent phases were examined for radioactivity by liquid scintillation counting techniques (LSC). Characterization and identification of the residue components were performed with thin layer chromatography and radiometric techniques. The presence of reincorporated C^{14}-activity was determined by hydrolysis of starch in the grain. The resulting C^{14}-labelled sugar molecules were derivatized to osazones which were further characterized by mass spectrometric analyses.

At one month after treatment plants had total radioactivity equivalent to 2.5 ppm terbufos. At two months total activity was equivalent to 1.0 ppm in the plants. At harvest (4 months after treatment) the plants had residue levels of 0.9 ppm, and the grain had residue levels of 0.09 ppm.

Radioactivity in the one month plant samples was characterized, and the components were identified. The residue consisted of the parent compound terbufos (CL 92,100 - 0.015 ppm) and its metabolites: terbufos sulfoxide (CL 94,301 - 0.182 ppm); terbufos oxygen analog sulfoxide (CL 94,365-0.058 ppm); terbufos sulfone (CL 94,320 - 0.024 ppm); CL 99,875 (0.018 ppm); CL 99,843 (0.011 ppm); and the terbufos oxygen analog suflone (CL 94.302-0.004 ppm). The identified components accounted for about 15% of the total radioactivity in the plant at one month after treatment.

At least 7 unidentified components were present in the one month plant residue and comprised about 4.5% of the total radioactivity.

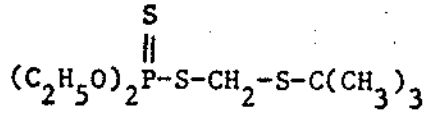
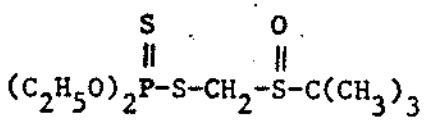
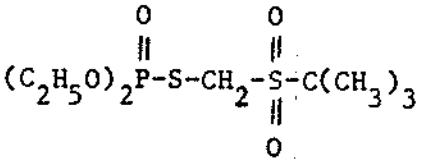
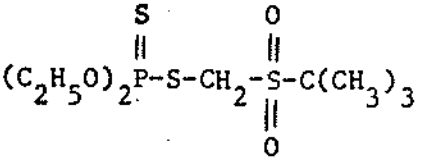
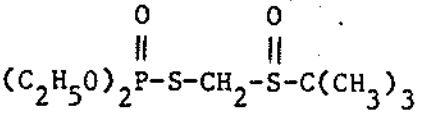
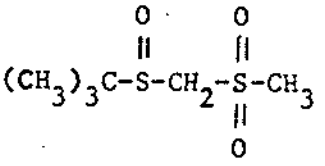
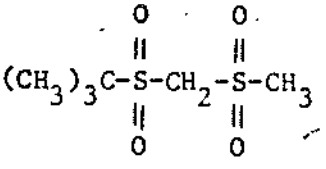
At least 69% of the radioactivity in plants was water-soluble. The study indicates that this activity consisted of alkylphosphates, sulfur-containing components, and reincorporated C^{14}-activity. The metabolic picture is similar for the two-month plant samples.

The metabolic behavior noted for terbufos in sorghum is similar to the metabolism of terbufos in corn (PP#3G1340, PP#4F1496). Moreover, this metabolic behavior of terbufos is generally characteristic of organophosphorus pesticides.

We have discussed the metabolism of terbufos in animals in PP#4F1496. The nature of animal residues is similar to that of plant residues.

We conclude that the nature of terbufos residues in plants and animals is adequately understood. The components of concern in the residues are terbufos and its cholinesterase-inhibiting metabolites: terbufos sulfoxide; terbufos sulfone; terbufos oxygen analog and its sulfoxide and sulfone. These components are determined by the analytical method.

Table of Compounds

CL Number	Chemical Name	Structure
92,100	O,O-diethyl-S-t-butyl-thiomethylphosphoro-dithioate	
94,301	Phosphorodithioic acid, S-(t-butylsulfinyl) methyl O,O-diethyl ester	
94,302	Phosphorothioic acid, S-(t-butylsulfonyl) methyl O,O-diethyl ester	
94,320	Phosphorodithioic acid, S-(t-butylsulfonyl) methyl O,O-diethyl ester	
94,365	Phosphorothioic acid, S-(t-butylsulfinyl) methyl O,O-diethyl ester	
99,843	Sulfoxide, t-butyl(methyl-sulfonyl) methyl	
99,875	Sulfone, t-butyl(methyl-sulfonyl) methyl	

Analytical Method

A ground sample is extracted by blending with methanol in chloroform, filtering, and evaporation of an aliquot of the filtrate. The residue is taken up with hexane, partitioned into acetonitrile, and the acetonitrile phase is evaporated.

The residue is taken up with acetone, treated with charcoal, filtered, and evaporated. The residue is taken up with chloroform and treated with metachloroperbenzoic acid. (The acid oxidizes residue components to the oxygen analog sulfone.) The solvent is evaporated, and the residue is taken up with acetone, cleaned up with precipitating solution, and cleaned up on a celite column.

The residues are extracted into chloroform and evaporated. The residues is taken up with acetone and determined by gas chromatography using a flame photometric detector in the phosphorus mode.

Untreated (control) samples of sorghum forage and grain had less than 0.03 ppm terbufos-equivalent residues. Control grain and forage samples were fortified with terbufos and its sulfoxide and sulfone, and terbufos oxygen analog and its sulfoxide and sulfone at levels of 0.05-0.50 ppm. Recoveries averaged 90-131%.

The analytical method has been successfully tested by EPA on corn grain and forage samples with terbufos and its oxygen analog sulfone metabolite at levels of 0.05 ppm and 0.10 ppm (PP#4F1496, G.P. Makhijani).

The analytical method is adequate for enforcement of the proposed tolerances for sorghum and sorghum forage.

Residue Data

Samples were obtained from crops in Colorado, Kansas, Nebraska, Oklahoma, and Texas. The crops were grown in soils treated as proposed, and samples were collected at intervals of 27-175 days after treatment (PHI).

The sorghum grain had no detectable residues (<0.05 ppm) due to the proposed uses and at PHIs of 95-175 days.

The sorghum forage had residues of <0.05 ppm at 27 days due to the proposed rates (1.2-2.4 oz act/1000 ft of row). Residues were 0.17-0.48 ppm at 48 days, <0.05-0.11 ppm at 60-70 days, and <0.05 ppm at 95-175 days due to the proposed use and rates.

In-furrow treatments were also submitted using the proposed banded rates. The in-furrow treatment is not proposed, but is submitted for informational purposes. The grain had no detectable residues (<0.05 ppm) at PHIs of 95175 days. Residues were 0.35-0.37 ppm at 27 days, 0.05-0.59 ppm at 48 days, <0.05-0.80 ppm at 60-70 days, and <0.05-0.14 ppm at 95-175 days.

Sorghum would not likely be grazed in an immature state or ensiled when immature because of the problem of prussic acid poisoning from feeding immature sorghum foliage to livestock. Sorghum could be used for forage at about 100 days after planting.

Residues of terbufos in or on sorghum grain or sorghum forage are not likely to exceed the proposed tolerances form the proposed use.

No residue data are submitted for sorghum grain fractions. The analytical data for sorghum grain do not indicate any instrument response for treated grain samples; detectable residues are not expected in grain. Therefore, we would not expect any residues in sorghum grain fractions.

Meat and Milk

Sorghum grain and forage are livestock feed items. Maximum terbufos ingestion levels can be estimated by using the proposed tolerance levels and the dietary levels for the various livestock. The maximum ingestion levels are: cattle (0.25 ppm); poultry (0.03 ppm); hogs (0.15 ppm); goats and sheep (0.2 ppm); horses (0.01 ppm).

Feeding studies were submitted in PP#3G1340 (cattle) and PP#4F1496 (chickens). Lactating cows were fed terbufos residues at a level of 2 ppm daily for 21 days. No residues were noted in milk (<0.01 ppm) or meat (<0.05 ppm). Laying hens were fed terbufos daily at a level of 2 ppm for 21 days. No residues were noted in eggs or meat (<0.05 ppm).

The absence of residues in eggs, milk, and meat in the feeding studies at a level of 2 ppm indicates that no residues are likely to occur in eggs, milk, meat, fat, or meat byproducts of livestock due to the proposed tolerance levels [§180.6(a)(3)].

TS-769:RCB:A. Smith:gs:X77377:RM810:CM#2:11/30/81
cc: RF, Circ., A. Smith, Watts, FDA, TOX, EEB, EFB, PP#1F2540
RDI: Quick, 11/25/81: Schmitt, 11/25/81

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Terbufos

PETITION NO. 1F2540

CCPR NO.

Codex Status

/ X / No Codex Proposal Step 6 or above

Proposed U.S. Tolerances

Residue (if Step 9):

Residue: S-[[(1,1-dimethylethyl)thio]methyl] O,O-diethylphosphorothioate and its cholinesterase-inhibiting metabolites

Crop(s)	Limit (mg/kg)
None	

Crop(s)	Tol. (ppm)
sorghum grain	0.05
sorghum forage and fodder	0.5

CANADIAN LIMIT

Residue:

Crop	Limit (ppm)
None on above commodities	

MEXICAN TOLERANCIA

Residue:

Crop	Tolerancia (ppm)
None	

Notes: