PP# OF0862

Petitions Control Branch and
Division of Pharmacology and Toxicology

October 6, 1969

Petitions Evaluation Branch,
Division of Pesticides

AF 9-577

OF0862/FAP# OH2445. Trifluralin in peppermint and spearmint hays and oils. Evaluation of analytical methods and residue data.

The Elanco Products Company proposes tolerances for residues of the herbicide trifluralin, (α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine), at 0.05 ppm in or on peppermint, peppermint hay, spearmint, and spearmint hay. The petitioner also proposes a food additive tolerance of 2 ppm for residues of trifluralin in peppermint oil and spearmint oil.

Tolerances have been established for residues of trifluralin on a variety of crops at 0.05-1 ppm.

Conclusions

1. The metabolism is adequately understood.

2. Adequate analytical methods are available for enforcement of the proposed tolerances.

3. Residues of trifluralin in or on peppermint and spearmint, or peppermint and spearmint hays, would not exceed the proposed tolerance from the proposed use. In the interest of maintaining uniformity with previously established tolerances we recommend that the tolerance proposals for the mint crops should be in terms of the hays.

4. Residues of trifluralin in peppermint or spearmint oils would not exceed the proposed 2 ppm food additive tolerance from the proposed use on the mint crops.

5. There is no reasonable expectancy of residues in meat, milk, poultry, and/or eggs from the feed use of treated crops for which tolerances have been proposed [Section 120.6(a)(3)].

6. Trifluralin is persistent in soils. However, the label restrictions on the rotation of certain crops, alleviates our concern over the possibilities of illegal residues in follow-up crops.

Recommendations

Pharmacological considerations permitting, we recommend for the establishment of a 0.05 ppm tolerance for residues of trifluralin in or on peppermint hay and spearmint hay. The basis for this recommendation is that the mint hay is the raw agricultural commodity and consequently the item on which the tolerance should be established. We also recommend, pharmacological considerations permitting, that the proposed 2 ppm food additive tolerance for residues of trifluralin in peppermint oil and spearmint oil be established.

Detailed Considerations

Proposed Use

Trifluralin is formulated as Treflan® E. C. (1 lb. act/quart), an emulsifiable concentrate containing 44.5% active ingredient. The formulation is proposed for use in the western United States for the control of annual grasses and broadleaf weeds.

Trifluralin is to be applied to established dormant peppermint and spearmint at broadcast spray application rates of 0.5-0.75 lb act/A, depending upon the soil type, and incorporated into the soil. For band applications, proportionately less is to be applied. There is no direct limitation on the number of applications; however, the fact that application is to dormant mint would seem to indicate a single application is to be made.

The label bears the following restrictions: Do not plant sugar beets, red beets, other root crops or spinach for 12 months after Treflan application. Do not plant sorghum (milo), corn or oats for 14 months after Treflan application. Do not plant any of these crops for 18 months after an application of Treflan to land that has not been irrigated.

[redacted] Sufficient information is not available to determine whether or not these ingredients are cleared under 120.1001.

Nature of the Residue

We have fully discussed the degradation of trifluralin in previous reviews.(5,6) Trifluralin is absorbed and translocated in plants. The major degradation routes appear to be through dealkylation and reduction, with the rate of degradation varying with the plants

Residues in carrots (roots and tops), grown in soil treated with ^{14}C-labelled trifluralin, consisted primarily of the parent compound, trifluralin (about 80%), with the chief metabolite as the monopropyl derivative after 110 days.(3,4)

Soybean and cotton plants(3,6), grown in soil treated with ^{14}C-labelled trifluralin, showed a distribution of radioactivity throughout the plants. No trifluralin or its initial degradation products (either the monoalkyl, or the reduced derivative) were noted. However, small amounts of $C^{14}O_2$ were liberated by the soil and plants. Radioactivity in the cottonseed was equivalent to 0.025 ppm trifluralin. The trifluralin residues in these plants had apparently been metabolized beyond the initial dealkylated and reduced products.

Immature peanut and sweet potato plants were grown in solutions of ^{14}C-labelled trifluralin for 72 hours.(7) Unchanged trifluralin accounted for <1% of the radioactivity in peanut plants. The major identifiable metabolite(the monopropyl derivative) was about 1.2% while the greater portion of the radioactivity (>96%) in peanut plants were more polar uncharacterized compounds. Sweet potato plants, however, had about 17% unchanged trifluralin, with about 65% of the residue as uncharacterized polar products, and about 16% unidentified components.

We have no studies on the metabolism of trifluralin in the mints; however, we believe the metabolic behavior exhibited in the above studies can be extended to include spearmint and peppermint in particular and plants in general.

Animal feeding studies (PP #7F0565) indicate that trifluralin is rapidly metabolized and excreted, with no significant storage of residues.

The metabolism of trifluralin is adequately understood.

Analytical Methods

Residues in peppermint and spearmint plants are determined using an electron capture gas chromatographic procedure (General Procedure 5001210). The macerated sample is extracted with methanol, filtered, and the resulting filtrate is extracted with methylene chloride. The extracts are evaporated and the residue is dissolved in n-hexane and cleaned up on a Florisil column. The eluate is evaporated, the residue dissolved in benzene, and an aliquot is injected into the gas chromatograph.

Untreated (control) mint samples (peppermint or spearmint) and one spent hay sample had trifluralin equivalent residues of NDR*-0.012 ppm. One aberrant value of 0.031 ppm was also noted. These control values were derived from a peak whose retention time coincided with that of the trifluralin peak. However, the control peak is not expected to interfere with the determination of trifluralin residues at the proposed tolerance level (0.05 ppm). Moreover, a thin-layer chromatographic method is available as a confirmatory procedure (Procedure 5801110). Control mint samples were fortified at 0.010 ppm with trifluralin. Recoveries were 67-127%, and are considered adequate.

Considering control and recovery values, the analytical method is sufficiently sensitive for trifluralin residue determinations at the proposed tolerance for mint and mint hay.

The analytical procedure was tested by DFCT and District laboratories on cucumbers and carrots at fortification levels of 0.05-1.5 ppm with favorable results.(8) We believe the results can be extended to include peppermint and spearmint hays. Therefore, a method tryout is not recommended.

The analytical procedure, with the TLC confirmatory procedure, is adequate for the enforcement of the proposed tolerance (0.05 ppm) on mint hays. These methods are published in the FDA, PAM, Volume II. Recent work in RCB has also shown that trifluralin is recovered in the 6% elution of the MOC method, PAM I. The results of this study will be reported in a L. I. B.

Residues of trifluralin in mint oils are determined by gas chromatography employing an electron capture detector, as in the determination of residues in the mint plants. However, a different extraction procedure is provided (General procedure 5801577). A sample of oil is extracted using an alumina column and hexane solvent. The eluate is concentrated and partitioned with hexane on the Florisil column included in the method for mint plants. The eluate is evaporated, the residue dissolved in benzene, and the trifluralin content determined by gas chromatography.

Control mint oil samples showed no detectable residues. Fortifications at 1 and 2 ppm yielded recoveries of 82-107%. The method is sufficiently sensitive for residue determinations in mint oils at the proposed tolerance (2 ppm).

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* NDR - no detectable residues

The petitioner states that a control sample is required to correct for background interferences, if any. Controls are not available to the field districts; however, the above mentioned thin-layer chromatographic procedure used in combination with the GLC method should be adequate for removal and/or correction of background interferences.

The method for oil is brief and simple, and involves only two steps, one of which has been tested (as part of a method) and found adequate. We can forsee no particular difficulty arising from the use of the untested alumina column step. Consequently, we believe the method to be satisfactory for trifluralin residue determinations in mint oils, and we are not recommending a method tryout.

Adequate analytical methods are available for the enforcement of the proposed tolerance for mint oils.

Residue Data

Mint plants (peppermint, or spearmint)

Samples were obtained from crops grown in the general area of proposed use (Western U. S.), which had been treated in the proposed manner (post plant, soil incorporated spray applications at broadcast rates of 0.5-0.75 lb act/A as well as exaggerated rates of 1.5 lb act/A), and harvested at intervals of about 90-170 days following treatments. Two samples were submitted which had received two applications (a single application in the previous year as well as one in the current year) at rates of 0.75 and 1.5 lb act/A respectively and harvested at intervals of about 90 and 135 days following the last treatment. Two peppermint samples which had received preplant applications at rates of 1and 2 lb act/A, and harvested at about 180 days after treatment were also submitted. Additionally, two samples of spent peppermint hay derived from crops which had been treated in the proposed manner at broadcast rates of 0.5 lb act/A, and the exaggerated rate (2x) of 1.5 lb act/A were submitted.

All samples had trifluralin residues of $\leq$0.030 ppm.

We conclude that residues of trifluralin in or on peppermint and spearmint, or peppermint and spearmint hays, are not likely to exceed the proposed tolerance (0.05 ppm) from the proposed use.

It is the current practice to consider the peppermint, or spearmint hay as the raw agricultural commodity. Tolerances for the mint crops should be in terms of the hays.

Mint oils - samples of spearmint oil, derived from plants which had received single applications at rates of 0.75 and 1.5 lb act/A and harvested at about 140 days from treatment, had trifluralin residues of 0.64-1.23 ppm. Two additional samples of spearmint oil were derived from plants which had received two applications (one in 1967, and repeated in 1968) at rates of 0.75 and 1.5 lb act/A respectively and harvested at about 166 days from the last application. The samples showed trifluralin residues of 0.57 ppm and 1.71 ppm, respectively. Peppermint oil, derived from plants which had received single applications at 0.75 and 1.5 lb act/A and sampled at about 140 days from the treatment, had trifluralin residues of 1.21 ppm and 1.04 ppm, respectively.

We conclude that residues of trifluralin in mint oils would not exceed the proposed food additive tolerances from the proposed use on the mint crops.

Meat and Milk

Spent hay may occasionally be fed to livestock, though not usually to dairy animals. Feeding studies (PP #7F0565) indicate that up to 10 ppm trifluralin in the diet would result in no detectable residues (<0.01 ppm) in the milk of cattle, goats, or sheep. We have concluded (see Nature of the Residue) that trifluralin is rapidly metabolized and excreted by animals (ruminants and non-ruminants) with no indicated tissue storage of residues. As a result, we expect no residues of trifluralin in meat, milk, poultry, and/or eggs due to the proposed tolerances [Category 120.6(a)(3)].

Soil Persistence

Soil dissipation studies with trifluralin under field conditions showed a decrease to a concentration of 10-15% within 6-12 months following application[1,3] Soil samples (sandy loam, sandy clay loam, silt loam, silty clay loam, and clay loam) were collected from 107 locations throughout the U.S. following commercial broadcast applications of trifluralin for 1-4 years, consecutively. Examination of the samples showed the trifluralin remaining ranged from about 0.5-31% of the amount applied, with most less than 10%.

The data suggest that trifluralin is persistent in soils; however, the petitioner has imposed label restrictions on the rotation of certain crops (see Proposed Use). Such restrictions alleviate our concern over the possibility of illegal residues in follow-up crops.

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