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PP#4G1501. Trifluralin on asparagus. Evaluation of the analytical method and residue data.

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Coordination Branch
and Toxicology Branch, RD

The Elanco Products Company proposes a tolerance for negligible residues of the herbicide ~~α~~α,α, -trifluoro-2,-6, dintro - N,N-idpropyl-p-toludine (trifluralin) in or on asparagus spears at 0.05 ppm.

Tolerances for trifluralin have been established on a variety of crops at levels ranging from 0.05 to 1 ppm. (Section 180.207). PP#4E1509 proposing a tolerance for negligible residues of 0.05 ppm in or on field corn grain, fodder and forage is also pending.

In the proposed experimental program, 100 lbs. of trifluralin (25 gals. of formulation) are to be applied to no more than 50 acres in the State of California. The experimental programs involves approximately 0.2% of the asparagus crop.

Conclusions

1a. We consider the fate of trifluralin adequately delinated for the purpose of the proposed temporary tolerance. It is our judgement ~~that~~ trifluralin per se is the principal residue of concern.

b. For a future permanent tolernace, or for a significantly larger experimental program in the event of a extension of the temporary tolerance, investigations to determine whether or not nitrosobenzanene or nitrosoamine derivatives are formed either on aerial parts of the plant or in soil will be required.

c. If either of these compounds are detected at significant levels (greater than 0.01 ppm) in the studies required in (b) above, adequately validated methodology and residue data for the detected compounds will also be required for a future permanent tolerance.

2. We consider the proposed method adequate to enforce the proposed temporary tolernace.

3a. The residue data are adequate to demonstrate that trifluralin residues will not exceed the proposed 0.05 ppm tolerance.

b. For a future permannent tolernace, data reflecting residue levels resulting from repeated annual applications will be required.

4. The proposed use will fall under Category 3 of Section 180.6(a) with respect to meat, milk, poultry and eggs.

Recommendation

1. We recommend that the proposed tolerance be established. We also recommend that it be expressed as a tolerance for residues of trifluralin in or on asparagus instead of asparagus spears.

2. For a future permanent tolerance or for a significant increase in the size of the experimental program. in the event of an extension of the temporary tolerance, the following will be required:

a(1). Studies determining whether or not nitrosobenzene derivatives (i.e., 6-nitroso-4 trifluoromethyl-2,nitroaniline) are formed in soil or aerial parts of asparagus treated with trifluralin and exposed to sunlight.

(2) If nitrosobenzene residues are actually formed, experimental data investigating the possibility of absorption, translocation and conjugation of these residues will also be required.

b(1) Studies determining whether or not nitrosoamine derivatives (i.e., N-nitroso-N-isoprppyl-4 trifluoromethyl-2,6-dinitroaniline) are formed in nitrate treated soils. Experiments should be conducted on soils of varying acidity and under aerobic and anaerobic conditions.

(2) If nitrosoamine residues are found at significant levels(above 0.01 ppm), data determining the residue levels that will result in treated asparagus will also be required.

c. Adequately validated methodology for the determination of nitrosobenzene or nitrosoamine derivatives in treated asparagus will also be required if these compounds are detected in treated asparagus.

d. Residue data reflecting repeated annual applications of trifluralin.

Detailed Considerations

Formulation

Trifluralin is marketed as an emulsifiable concentrate under the trade name, Treflan E.C., containing 44.5% technical trifluralin (4 lbs/gal) [redacted]

The components of [redacted] are cleared under Section 180.1001.

As discussed in Dr. R. Hummel's memo of 6/1/72 "Nitrosoamines in Dinitroanaline Herbicides", trifluralin is synthesized by [redacted]

We therefore reiterate our previous conclusion that there is no expectation of nitrosoamine formation during the synthesis of trifluralin.

INERT INGREDIENT INFORMATION IS NOT INCLUDED

MANUFACTURING PROCESS INFORMATION IS NOT INCLUDED

Proposed Use

Trifluralin is to be applied at rates of 0.5 to 2 lbs. act/acre on a broadcast basis. Depending on soil texture. The highest recommended rate is expected to be [illegible] act/acre; however, 2 times this rate are proposed for the temporary tolerance in order to obtain additional residue data.

Applications are to be made after the last cutting but before ferning. No restrictions against the use of treated asparagus as a feed item has been imposed.

Nature of the Residue

The fate of trifluralin in both plants and animals has been discussed in detail in our review of PP#7F0555 and PP#7G0533 (see memo's of 5/24/67 by R. Arnold and Jack Wolff, 10/31/66 by T. Woodward, respectively). Trifluralin is absorbed by and translocated in plants. The route of degradation appears to be through dealkylation and reduction with the rate of degradation varying with the plant. Residues in carrots (roots and tops) grown in soil treated with C^{14} labeled trifluralin consisted of primarily parent compound (about 80% with the chief metabolite as the monopropyl derivative after 10 days.

Soybean and Cotton plants growing in C^{14} labeled trifluralin treated soil showed a distribution of activity throughout the plant. No trifluralin or its initial degradation products were detected. Small amounts of radiolabelled carbon dioxide were liberated by both the soil and plants. Radioactivity in cottonseed was equivalent to 0.025 ppm. The data indicate that the trifluralin ring structure was apparently catabolized to carbon dioxide by both soil microbes and by cotton an soybean plants.

Immature peanuts and sweet potatoes were grown in solutions containing C^{14} labeled trifluralin for 72 hours. Trifluralin per se accounted for <1% of the total activity in peanut plants. The major identifiable metabolite, the monopropyl derivative, comprised about 1.2% of the activity while greater than 96% of the activity was characterized as more polar degradation products. Sweet potato plants, however, had about 17% unchanged trifluralin, 16% unidentified organic soluble metabolites and approximately 65% polar metabolites.

Studies have also been done showing the photodegradation of the dinitroaniline upon exposure to ultraviolet light, (telecon with Dr. J. Plimmer of USDA). The proposed use envolves the application of trifluralin after the last cutting of spears, thus aerial portions of the plant could be exposed to the solution spray. At the present time, no information is / to determine whether nitrosobenzenes are formed under field conditions, nor is any data available to determine whether or not these residues if formed will be absorbed and translocated to edible portions of the plant.

Because of the limited nature of the experimental program, it is our judgment that these questions need not be resolved for the purpose of this temporary tolerance proposal. However, for a future permanent tolerance (or for a significantly larger experimental program) experimental data determining whether or not residues of nitrosobenzenes are formed on asparagus under field conditions will be required. If nitrosobenzenes are actually formed, experimental data investigating the possibility of absorbtion, translocation and conjugation of nitrobenzene residues should also be submitted.

As discussed above, dealkylation of trifluralin to yield the secondary amine is the primary route of degradation. The presence of secondary amines in nitrite treated soils gives rise to at least a remote possibility that nitrosoamine derivatives of trifluralin could be formed in nitrite treated soils. Data have been submitted in petitions PP#2G1285 and PP#4F1431 showing that nitrosamines are not formed when s-ethyl,dipropylthiocarbamate, dibutalin (a dinitroanaline herbicide) is added to nitrite treated soils. These data indicate that nitrosation of trifluralin's amine group is unlikely and we therefore will not require any additional data for the purpose of this temporary tolerance proposal. However, for a future permanent tolerance or for a significantly larger experimental program, data determining whether or not nitrosoamine derivatives of trifluralin are formed in nitrite soils will be required. Dr. P.C. Kearney of USDA indicated that he originally had intended to investigate this question but budget considerations had forced to indefinately postpone the work. He further indicated that he would be very interested in the results of these experiments when they become available. Experiments should be conducted on soils of varing acidity and under aerobic and anaerobic conditions. Further, if nitrosoamines are found in soils at significant levels (above 0.01 ppm), data determining the residue levels that will result in treated asparagus will also be required.

In conclusion, we can consider the fate of trifluralin adequately delineated for the purpose of this temporary tolerance proposal. Trifluralin is degraded to carbon dioxide by both plants and soil microbes, although significant residues of trifluralin and its mono-isopropyl derivative may be found in certain roots crops. However, for a future permanent tolerance or for a significantly larger experimental program in the event of a extension of the temporary tolerance, the questions concerning the formation and fate of the nitrosobenzene or nitrosamine derivatives will have to be resolved.

Analytical Method

Trifluralin residues are determined using an electron capture gas chromatographic procedure #5801616 (which superceded procedures #58021210 and #58001110). Macerated plant material is extracted with methanol, filtered and the resulting filtrate partitioned against methylene chloride. The methylene chloride layer is then evaporated to dryness and the residue dissolved in hexane and chromatographed on a florisil column. The eluate is evaporated to dryness and diluted to a specific volume and determined by gas chromatography.

The proposed analytical method is essentially the same the procedure successfully tested in our laboratories on cucumbers and carrots at levels of 0.05 and 1.5 ppm respectively. The petitioner reports recoveries of approximately 85% from asparagus fortified at 0.05 and 0.1 ppm. All control reported were less than 0.01 ppm. We consider the method validation data submitted adequate for the purpose of this temporary tolerance. However, for a future permanent tolerance data (including representative chromatograms) from individual control and recovery experimental will be required.

As discussed in the Nature of the Residue section above, the question of whether or not nitrosobenzene or nitrosoamine derivatives result in asparagus from the proposed use will have to be resolved for a future permanent tolerance. If these additional data indicate that either of these types of compounds are formed, appropriate methodology and validation data for the detected compounds will be required for a permanent tolerance.

Residue Data

Residue data have been submitted from eight field experiments in which trifluralin was applied to established asparagus at rates fo 0.5 to 2.0 lbs/acre. Samples of spears were taken 4 to 8 weeks after treatment Residue levels reported for all but two samples were below the limit of detection,,0.01 ppm. The values reported for the two remaining samples were 0.013 and 0.015 ppm.

Trifluralin is to be applied after the last cutting but before ferning, thus, effectively limiting the number of applications to one per season. The use also involves a built in PHI during the ferning period (and during the dormant period, if any) of at least 8 to 10 weeks. Some of the data reported reflects samples that were apparently treated before the last cutting and subsequently harvested. We would expect these samples to have higher residues. However, no data have been submitted that reflects repeated annual applications. For the purpose of this temporary tolerance, we can consider these data adequate to demonstrate that residues of the parent compound resulting from the proposed use will not exceed the proposed 0.005 ppm tolerance level. However, for a future permanent tolerance additional data reflecting repeated annual applications will be required.

Meat, Milk, Poultry and Eggs

The proposed use involves no feed items and therefore it falls under Category 3 of Section 180.6(a) with respect to meat, milk, poultry and eggs.

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