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Petitions Control Branch and
Division of Toxicological Evaluation

Pesticides Branch, Division of Food
Standards and Additives

AF 9-577

PP #7F0588. Benefin on various commodities. Evaluation of analytical method and residue data.

The Blanco Products Company proposes a tolerance of 0.05 ppm for residues of the herbicide, Benefin (N-butyl-N-ethyl-p,p-trifluoro-2,6-dinitro-p-toluidine, trade name Balan) in or on alfalfa, bird's-foot trefoil, alsika clover, ladino clover and red clover.

A tolerance of 0.05 ppm for residues of Benefin in or on peanuts was established in connection with PP #7F051A. A tolerance is proposed for direct seeded lettuce in pending PP #7F0610. A petition (PP #7F0565) for a tolerance for the closely related herbicide, trifluralin, on alfalfa is also pending.

Conclusions

1. While we have no metabolic data for Benefin, DTS has stated that, because of its close similarity to trifluralin, there was no need for specific metabolic data for Benefin. The metabolic routes are considered to be the same.
2. The gas chromatographic method utilizing electron capture detection is adequate for determining residues of Benefin at the proposed tolerance level on both the fresh commodity and the hay. A TLC clean-up modification makes it specific and adequate for enforcement purposes.
3. When Benefin is used as directed, residues in or on fresh alfalfa, bird's-foot trefoil, the clovers and their respective hays would not exceed the proposed 0.05 ppm tolerance.
4. Establishment of the proposed tolerances would not result in any detectable residues of the order of less than 1 ppb Benefin in meat, milk, poultry and eggs.
5. We would expect Benefin to be persistent in soil and, without a label restriction, there could be a problem of illegal residues occurring in certain follow-up crops.

Recommendations

Pharmacological considerations permitting, we recommend establishment of a 0.05 ppm tolerance for residues of Benefin in or on alfalfa, bird's-foot trefoil and clover.

In order to avoid a proliferation of commodities, the petitioner should be asked to modify his Section F and change his request for a tolerance on alsike clover, ladino clover and red clover to a request for a tolerance on clover (unqualified as to variety).

We recommend that PHD, USDA be consulted as to the possible need of a label restriction for certain follow-up crops in Benefin treated soils.

The contemplated tolerances of 0.1 and 0.4 ppm for residues of trifluralin in or on fresh alfalfa and alfalfa hay respectively are not in conflict with the proposed 0.05 ppm tolerance for Benefin in or on alfalfa. The proposed use for trifluralin on alfalfa is for application to established alfalfa whereas the proposed use for Benefin is for a preplanting application. Consequently we would expect higher residues to result from the trifluralin usage than from this Benefin usage.

Detailed Considerations

Proposed Use

Benefin is formulated as a 1.5 lb active/gal. concentrate.

It is to be applied broadcast and incorporated into the soil at rates of 0.75-1.5 lb act/A. The lower rates of application are for lighter soils and the higher rates for heavy soils.

It is to be used within three weeks before planting. There is a label restriction against application after planting.

Nature of the Residue

No metabolic data have been submitted for Benefin. However, by its memo of November 2, 1966, DTE stated that, because of its close similarity to trifluralin, there was no need for specific metabolic data for Benefin.

The metabolic fate of trifluralin has been discussed in detail in our review of PP #7F0355 dated 5/24/67. The major metabolic routes are the same for both chemicals and involve despropylation and reduction.

Residue Method

A gas chromatographic method (General Procedure 5301230) utilizing electron capture detection is used for determining residues of Benefin. It is identical to the method for trifluralin.

The sample is finely ground and extracted with methanol. Benefin is extracted from the methanol into methylene chloride, the methylene chloride evaporated and the residue taken up in n-hexane which is cleaned up on a Florisil column. The fraction of the eluate containing Benefin is evaporated to dryness and the residue taken up in benzene. An aliquot of the benzene is injected into the gas chromatograph.

Ethion, BHC and zineb interfere with the GLC method. Procedure 5801110 (discussed in our memo of 5/24/67, PP 470555) utilizes a TLC clean-up step which would eliminate these interferences. Thus, the GLC method with the incorporation of the TLC procedure becomes quite specific for Benefin.

Trifluralin would, if tolerances for trifluralin were to be established in the future on the subject crops (at present trifluralin is registered only for alfalfa (seed) on an N.A. basis), probably interfere with this GLC-TLC method for Benefin. However, if this situation did arise, the petitioner does have a separation technique whereby these two herbicides could be identified. This technique utilizes TLC on aluminum oxide in either a n-hexane or a n-pentane system.

Validation data are reported for all the subject crops. Control values for all of these ^{at 0.01 ppm} fortified at 0.01 ppm vary normally for this method and range from 60-120% with most values in the range of 68-100%. We consider these recoveries quite adequate in view of the low level of fortification. We have no validation data on this method for Benefin on hay. Such data are available, however, for the same method when applied to trifluralin on alfalfa hay (PP 470565). Recoveries for alfalfa hay fortified at 0.01 ppm ranged from 54-97% with all but one value in the range of 69-97%. Control values were less than 0.01 ppm.

We see no reason therefore why the method cannot be applied to the determination of Benefin on the Hays with a comparable sensitivity of 0.01 ppm.

The results of the method trial for Benefin on peanuts have been discussed in our memo of June 8, 1967 (see PP 470512A). Recoveries on peanuts fortified at the 0.05 and 0.10 ppm levels were 80% or better with or without the TLC (Procedure No. 5801110) cleanup. Several extraneous peaks were observed in the determination not utilizing TLC cleanup but none were recorded after the cleanup. Even so, control values in all cases were less than 0.005 ppm. Considering the satisfactory results obtained with a difficult

aily commodity such as peanuts, we did not recommend a method trial for any of the subject crops.

We conclude that the method with TLC cleanup is adequate to enforce the proposed tolerances.

Residue Data

Fresh Alfalfa

Geographical representation is adequate.

Data are submitted for application at the rate of 0.75 to an exaggerated 3.0 lb act/A. Preharvest intervals range from 66-314 days. In actual practice, alfalfa is ready for pasture in 4-5 months after planting and is harvested for hay at 85-130 days.

None of the values were corrected for blanks. All values reported are less than 0.01 ppm, within the sensitivity of the method. We conclude that residues from the proposed use on fresh alfalfa would not exceed the proposed 0.05 ppm tolerance.

Fresh Bird's-foot Trefoil and Clover (Alsike, Ladino and Red).

A limited amount of residue data are submitted for these commodities and the data submitted are not quite geographically adequate. However, because alfalfa is a related crop and because the alfalfa data show residues in line with those reported for bird's-foot trefoil and clover, we are applying the alfalfa data to these other crops.

Data are submitted for application at the rate of 0.75-3.0 lb act/A with preharvest intervals of 66-166 days. All values are reported as less than 0.01 ppm, within the sensitivity of the method.

We conclude that residues from the proposed use on fresh bird's-foot trefoil and clover would not exceed the proposed 0.05 ppm tolerance.

Hay (Alfalfa, Bird's-foot Trefoil and Clovers)

No residue data are submitted for these hays. However, if we use the residue values reported for the fresh commodities (all residues less than 0.01 ppm) and apply a dry-down factor of 4 (and assume no losses on drying), residues in the dried hay would still not exceed the proposed 0.05 ppm tolerance.

We can conclude that residues of Benefin in or on alfalfa hay, bird's-foot trefoil hay and clover hay which result from the proposed use would not exceed the proposed 0.05 ppm tolerance.

In summary, the residues of Benefin in or on alfalfa, bird's-foot trefoil and clover (the fresh commodities or their respective hays) from the proposed use would not exceed the proposed tolerance of 0.05 ppm.

Residues in Meat and Milk

Both the pasture and the hay of the subject commodities are important feed items for livestock. Dried alfalfa meal is also used as a supplement in poultry rations.

Limited data are available to indicate whether or not residues of Benefin would accumulate in meat and milk. A 90-day feeding study carried out on dogs fed Benefin at high levels showed some accumulation in the fat; a daily feeding level of 500 ppm resulted in residues in the fat of 3.0-7.1 ppm. In the same study, levels of 2000 and 8000 ppm daily resulted in residues in the fat of 19 and 37 ppm respectively. Assuming linearity, each ppm fed contributes 0.005-0.01 ppm to the fat.

A 23-day feeding study with 2 lactating goats was also conducted using Benefin at 1 ppm in the diet. Ring-labeled Benefin was fed on the ninth day only. Benefin was recovered in the feces and urine to the extent of 100.9% from one goat and 86.4% from the other. The petitioner stated that no significant amount of Benefin was found in milk. As we interpret the findings, there is a trace of activity (uncharacterized as to nature) in the milk after ingestion of the labeled Benefin.

In our opinion, the combined data show the possibility of very small residues in fat of meat and milk. When we translate the results of the feeding studies to the dairy cow and assuming linearity, we would estimate residues of about 0.2 ppb of Benefin and its possible metabolites in butterfat (less than 0.01 ppb in milk). Extrapolation of the dog data indicates only about 0.5 ppb in fat from the feeding of Benefin at the 0.05 ppm feeding level. Either level (0.2 ppb or 0.5 ppb) would be below the level of detection of the residue method.

Feeding studies with the closely related herbicide, trifluralin, showed that the feeding of 10 ppm trifluralin in the diet of ruminants would result in no transfer of residues to meat and milk.

ruminants

Because of the wide margin of safety, we applied the data to non-ruminants as well. We concluded that there would be no transfer of residues (less than 0.01 ppm) to milk, meat and eggs (J. Wolff memo 5/29/67, FP #770563).

Summarizing the feeding studies for Benefin and trifluralin, we conclude that non-detectable residues (less than 1 ppb) of Benefin would occur in meat, milk, poultry and eggs as a result of the proposed use.

Soil Persistence

Soil persistence data for trifluralin were discussed in our memo dated 10/31/66 (FP #760533 by T. Woodward). Trifluralin is relatively persistent in soil, but with label restrictions as to the rotation of crops, we believe that there would be no problem of residues in certain follow-up crops. Since Benefin is structurally very similar to trifluralin, Benefin residues would by analogy, be expected to persist in soil. We feel that FRD, USDA, should be consulted as to the need for a similar label restriction for Benefin.

Other Considerations

The petitioner has proposed a tolerance for clovers (alsike, ladino and red). We feel, that in order to avoid a proliferation of commodities, the petitioner should be asked to modify his Section V and change his request to one for clover (unqualified as to variety). The term clover would include the three varieties for which tolerances are proposed.

R. S. Quick

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