4-1-93

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

APR 1 1993

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Trifluralin Processing Study on Oranges (whole orange, dried pulp, wet peel, molasses, oil, and juice).
DP Barcode: D188347; CRBS No. 11430;
MRID No.:426426-01; Case No. 179

FROM: David J. Miller, Health Services Officer, USPHS
Special Review, Section I
Chemistry Branch II--Reregistration Support
Health Effects Division (H7509C)

THRU: Andrew Rathman, Section Head
Special Review, Section I
Chemistry Branch II--Reregistration Support
Health Effects Division (H7509C)

TO: Terri Stowe, PM Team 71
Reregistration Branch
Special Review and Reregistration Division (H7508W)

Treflan® is a preemergence herbicide which is incorporated into the soil to provide long-lasting control of many annual grasses and broadleaf weeds as they germinate. Treflan® 5 is recommended for application to the soil in vineyards and to the floors of citrus and nut groves as well as to orchard floors of many stone fruits. It is applied to the soil as a broadcast spray directed to the base of the trees and is currently registered for use on orange trees at 0.5-2.0 lb ai/A as a broadcast application that is incorporated into the soil.

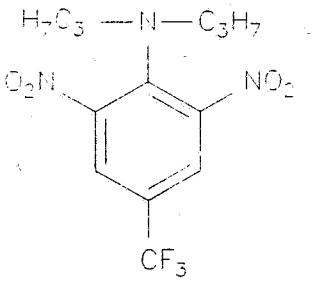
CBRS has been requested to review an orange processing study submitted to the Agency by DowElanco. This information was presented in two volumes: Volume 1 contains the transmittal document while Volume 2 contains the actual study which is entitled "Determination of Residues

of Trifluralin in Oranges and Processed Products Resulting from a Post-Plant soil Application of Treflan 5 Herbicide". In this study, Treflan® 5 (trifluralin) was applied to oranges grown in California at 1x, 3x, and 5x treatment rates in order to determine if processing of whole oranges containing the residues of trifluralin would concentrate in any of the processed products. Processed commodities which were analyzed were: dried pulp, wet peel, molasses, oil, and juice.

A tolerance of 0.05 (N) ppm has been established for residues of trifluralin per se in or on citrus fruit (40 CFR §180.207). The only food additive tolerances established for trifluralin are on peppermint and spearmint oils (40 CFR 185.5900). As there are no Codex MRLs for residues of trifluralin, there is no question with respect to Codex/U.S. tolerance compatibility.

The nature of the residue in plants and animals is adequately understood. The residue of concern in both plants and animals is trifluralin per se. Adequate analytical methods are available for enforcing trifluralin tolerances in plants. These methods are listed in PAM, Vol. II as Methods II and III.

The structure of trifluralin is presented below:



Trifluralin

CONCLUSIONS

1. The orange processing study is adequate. Residues of trifluralin in all processed commodities did not exceed the presently established tolerance (0.05 ppm) in orange commodities processed from oranges harvested at maturity following a post-plant application of trifluralin to the soil at 5x the maximum label rate. Although trifluralin was not applied at an exaggerated rate equivalent to the highest theoretical concentration factor (assumed to be 1000x for orange oil), the 5x rate used is sufficiently high. These data are therefore acceptable for assessing the potential for residues of trifluralin to concentrate in orange processed commodities. No food/feed additive tolerances are necessary for trifluralin residues in orange processed

commodities.

2. The GC/electron capture detector (ECD) method described in the current submissions, Eli Lilly Method AM-AA-CA-R023-AA-755, is adequate for collecting data on residues of trifluralin in whole oranges and in the associated processed commodities (i.e., dried pulp, wet peel, molasses, oil, and juice). Acceptable recoveries were found in all commodities.

3. The available storage stability data indicate that trifluralin is stable in whole orange and the processed commodities of dried pulp, wet peel, and juice for the intervals and conditions reflected in the current submissions. The submitted storage stability studies do not reflect the reported storage intervals for orange molasses or for orange oil: in the case of orange molasses, recoveries ranged from 60% (at 365 days) to 64% (at 146 days), while in the case of orange oil, recoveries ranged from 140-169%[1]. Nevertheless, given the fact that trifluralin has been found to be stable in numerous matrices (including soybean oil), CBRS concludes that the storage stability data are adequate (see Registration Standard Update 10/29/91).

RECOMMENDATIONS

CBRS recommends that the present processing study conducted with oranges be considered adequate for the entire citrus group. At an application rate of 5x, no overtolerance residues were seen in any processed commodity. CBRS believes that no significant additional information would be gained by requiring other processing studies on the two additional representative commodities in the citrus group, lemons and oranges.

DETAILED CONSIDERATIONS

Treflan® is a preemergence herbicide which is incorporated into the soil to provide long-lasting control of many annual grasses and broadleaf weeds as they germinate. It is applied to the soil as a broadcast spray directed to the base of the trees and can be applied at the maximum rate of two quarts per acre (2.5 lb ai/A) no less than 60 days before harvest. DowElanco's Treflan 5 trifluralin label indicates that trifluralin is currently registered for use on orange trees at 0.5-2.0 lb ai/A as a broadcast application that is incorporated into the soil.

A tolerance of 0.05 (N) ppm has been established for residues of trifluralin per se in or on oranges (40 CFR §180.207). The present study was conducted to determine if processing of whole oranges containing the residues of trifluralin would concentrate the residues in any of the processed dried pulp, wet peel, molasses, oil, or juice commodities to a level that would

---

[1] The registrant speculates that this sample was double-spiked.

exceed the established tolerance of 0.05 ppm trifluralin for the whole oranges.

Treatment and Sampling

Treflan® 5, a concentrated formulation containing five pounds of trifluralin per gallon as the active ingredient, was applied as a broadcast spray directed to the base of orange trees at an experimental site in Riverside, California. The test site consisted of both a control and treated plot. Treflan® 5 herbicide was incorporated into the soil prior to planting at 2.0, 6.0, and 10.0 lbs ai/acre, representing 1x, 3x, and 5x application rates, respectively. The applications were made in the early spring when the orange trees were in pre-bloom and new weed and grass growth was 2-6 inches tall. The broadcast spray was applied using a tractor-mounted pressurized boom sprayer, with the spray directed to the base of the tree trunk and out to the dripline in a nine-foot band. Immediately following application, the soil in the treated area was lightly cultivated with a small rototiller to incorporate the spray just beneath the soil surface.

Samples of mature oranges were collected from both the control and treatment plots at normal harvest, 63 days following herbicide application[2]. Since the oranges from the highest rate (10 lbs/acre) survived, samples were not collected from the two lower treatment rates. Each sample was comprised of 16 oranges, randomly selected from all parts of the middle four trees in each plot. The bulk samples for processing were collected in a similar manner from the same middle four trees. The bulk sample of oranges from the untreated trees totaled 1135 pounds and from the treated trees 1179 pounds.

Sample holding times, both from harvest to extraction and from processing to extraction, are presented in Table 1:

Table 1. Sampling, Processing, and Extraction Dates and Holding Times for Orange RAC and Processed Commodities.

Commodity	Sampling/ Harvest Date	Processing Date	Extraction Date	Processing to Extraction Time (days)	Total Storage Time (days)
Whole Oranges	6/01/90	--	4/01/91	--	304
Dried Pulp	6/01/90	6/02/90	4/01/91	303	304

[2] CBRS notes that the label instructions indicate that harvest can take place 60 days following application. In this study, harvest occurred 63 days following application. CBRS does not feel this additional three days is significant.

Table 1. Sampling, Processing, and Extraction Dates and Holding Times for Orange RAC and Processed Commodities.					
Commodity	**Sampling/ Harvest Date**	**Processing Date**	**Extraction Date**	**Processing to Extraction Time (days)**	**Total Storage Time (days)**
Wet Peel	6/01/90	6/02/90	4/04/91	306	307
Molasses	6/01/90	6/02/90	5/29/91	361	362
Oil	6/01/90	6/02/90	6/04/91	367	368
Juice	6/01/90	6/02/90	4/02/91	304	305

Residue Analytical Methods

The samples of whole oranges and orange processed products for residues of trifluralin essentially followed the procedures in DowElanco Method AM-AA-CA-R023-AA-755. This method is a modification of Procedure No. 5801616 which is a modification of Procedure No. 5801210 (PAM Volume II, Sec. 180.207 Method II). Modifications include differing dilution solvents and GC columns (per Registration Standard Update, 10/29/91, p. 5) The method determines residues of trifluralin in crops and soils with a method detection limit of 0.010 ppm. Trifluralin was extracted from each matrix with methanol. Cleanup of the extract was accomplished by diluting the extraction solvent with aqueous sodium chloride and partitioning that diluted extraction solvent three times with methylene chloride. Decane was added as a keeper solvent and the methylene chloride removed by vacuum rotary evaporation; the extract was reconstituted in hexane for further cleanup through a florisil column. Hexane was used for eluting the analyte and after vacuum rotary evaporation the residue was reconstituted with toluene for quantitation by gas chromatography with electron capture detection. The presence of trifluralin was confirmed by GC/MSD.

Method Validation

For method validation, control samples of each commodity were fortified with trifluralin at 0.01 ppm, 0.05 ppm, and 0.10 ppm. Sample calculations and chromatograms were provided with each study. Method recoveries of trifluralin from each rac and processed commodity are summarized in Table 2, on the following page.

Table 2. Recoveries of Trifluralin From Oranges and Their Associated Processed Commodities Fortified with Trifluralin at Levels of 0.01, 0.05, and 0.10 ppm.			
Commodity	**Fortification Level (ppm)**	**Number of Samples**	**Percent Recovery**
Whole Orange	0.01-0.10	7	89-120
Dried Pulp	0.01-0.10	7	110-118
Wet Peel	0.01-0.10	7	103-123
Molasses	0.01-0.10	7	110-115
Oil	0.01-0.10	8	71-97
Juice	0.01-0.10	7	79-109

These data indicate that the method used is adequate for collecting data on residues of trifluralin per se from oranges and from the dried pulp, wet peel, molasses, oil, and juice processed commodities.

Storage Stability Data

In conjunction with residue studies, DowElanco submitted data depicting the stability of trifluralin in oranges and associated processed commodities stored at approximately -20 °C for various intervals. As residue samples of the above commodities were placed into frozen storage at the analytical laboratory, control samples were fortified with trifluralin at 0.05 ppm. The spiking and extraction dates as well as the holding times for the fortified samples (i.e., the aged spikes) are presented in Table 3, while the recovery of trifluralin from fortified control samples and the storage intervals for actual residue samples are shown in Table 4.

Table 3. Fortification and Extraction Dates, and Holding Times for Whole Orange and Processed Commodities Fortified at 0.05 ppm.			
Commodity	**Fortification Date**	**Extraction Date**	**Storage Time[a] (days)**
Whole Oranges	8/03/90	4/01/91	241
	1/03/91	6/06/91	154

Table 3. Fortification and Extraction Dates, and Holding Times for Whole Orange and Processed Commodities Fortified at 0.05 ppm.			
Commodity	**Fortification Date**	**Extraction Date**	**Storage Time[a] (days)**
Dried Pulp	1/03/91	4/01/91	88
	1/03/91	11/26/91	327
Wet Peel	1/03/91	4/04/91	91
	1/03/91	11/26/91	327
Molasses	1/03/91	5/29/91	146
	1/03/91	1/03/92	365
Oil	1/03/91	6/04/91	152
	1/03/91	6/04/91	152
	1/03/91	4/14/92	467
Juice	1/03/91	4/02/91	89
	1/03/91	11/26/91	327
[a] Fortification to extraction interval--actual analysis of the sample may have occurred later			

The submitted storage stability data indicate that trifluralin is stable at -20 °C for at least 241 days in whole oranges; 327 days in dried pulp; 327 days in wet peel; and 327 days in juice. These data support the reported storage intervals for residue samples of whole oranges, dried pulp, wet peel, and juice.

Storage stability data in the current registrant submission are inadequate to support the storage intervals for molasses or oil[3]: recoveries are outside of CBRS guidelines which

---

[3] The laboratory reported spike recovery problems for the orange oil samples. Aged orange oil spikes recovered 168%, 156%, 169%, and 140% of the theoretical 0.05 ppm. The laboratory states that

> "A review of the spiking records indicates that the proper amounts of trifluralin solution was added to orange oil, while the recoveries indicate the aged orange oil spikes were double spiked. If all aged orange oil spikes were double spiked, the recoveries do not indicate extensive degradation of trifluralin but fail to support the theoretical level
>
> Evidently, the spiking records do not match the action performed when spiking these samples. While these exaggerated recoveries may cast doubt on the stability of trifluralin in orange oil in this study, trifluralin stability in frozen matrices has been demonstrated repeatedly. Other matrices in this study

prescribe recoveries of 70-120%.

Table 4. Stability of Trifluralin in Oranges and Associated Processed Commodities Fortified with Trifluralin and Stored at Approximately -20 C, Along with the Storage Intervals of Actual Residue Samples.

Commodity	Fortified Control Samples[a]		Residue Samples[b]
	Storage Interval[c] (days)	Recovery[d]	Storage Interval[e] (days)
Whole Orange	154, 241	85%, 102%	304
Dried Pulp	327, 88	90%, 102%	303
Wet Peel	327,91	96%, 85%	306
Molasses	365, 146	60%, 64%	361
Oil	152-467	140-168%	367
Juice	327, 89	112%, 118%	304

[a] Control samples were fortified with trifluralin at 0.05 ppm
[b] Residue samples were stored at -20 C
[c] Storage interval from harvest to sample extraction, from Table 3 of this document
[d] Corrected recovery in stored sample. This is calculated as to "fresh fortification recovery" ÷ "apparent recovery in stored sample"
[e] Storage interval from harvest to sample extraction, from Table 4 of this document

Magnitude of the Residue--Orange Processed Commodities

Following harvest, orange samples were either immediately frozen and shipped by freezer truck to ABC Laboratories (Columbia, Missouri) for preparation and determination of residues, or delivered for processing to California State Polytechnic University at Pomona

---

indicated trifluralin was stable in orange processed commodities. A stability study (ABC Study #35698) indicated trifluralin was stable in many frozen matrices for extended periods of time."

While the 10/91 Reregistration Standard Update contains no information regarding storage stability of oranges or any citrus crop, CBRS notes that the Trifluralin Registration Standard Update (dated October 29, 1991) concludes that trifluralin is stable in soybean oil for a period of at least 555 days. The Registration Standard Update also concludes that trifluralin is stable in a wide variety of crop matrices. On this basis, CBRS finds the storage interval of 367 days for the orange oil sample acceptable.

California on the same day as harvest[4].

Bulk orange samples were processed into dried pulp, wet peel, molasses, oil, and juice using a simulated commercial process. All samples were placed in freezers within 90 minutes of collection. Temperatures in the freezers ranged from a high of +5 F (as the samples were being placed into the freezers) to a low of -6 F.

After processing, samples were again frozen and shipped to the ABC Laboratories for residue analysis.

Trifluralin residues were determined at ABC Laboratories using DowElanco AM-AA-CA-R023-AA-755. A single control and treated sample were analyzed for each orange commodity. Residues of trifluralin in or on the whole orange rac and the dried pulp, wet peel, molasses, and juice processed commodities were nondetectable (<0.01 ppm). A residue level of 0.05 ppm was found in the oil processed commodity. Apparent residues of trifluralin were nondetectable in or on all control samples.

The registrant submitted no data which would allow calculation of the maximum theoretical concentration factors for dried pulp, wet peel, molasses, oil, and juice based on the weight of the whole orange and each of the resulting processed fractions. Thus, theoretical concentration factors for residues in peel, oil, and juice were taken from the CBRS/CBTS monograph entitled "Maximum Theoretical Concentration Factors" and dated January, 1993; these values are 3.3x, 1000x, and 2x, for peel, oil, and juice, respectively. No information is available to determine the Maximum Theoretical Concentration Factors for dehydrated pulp and molasses.

The orange processing study is adequate. Although trifluralin was not applied at an exaggerated rate equivalent to the highest theoretical concentration factor (assumed to be 1000x in oil[5]), the use of whole oranges bearing non-detectable residues following application of trifluralin at 5x the maximum label rate is acceptable, given that trifluralin residues in all processed commodities were at or below the tolerance level. These data are therefore acceptable for assessing the potential for residues of trifluralin to concentrate in orange processed commodities and no food/feed additive tolerances are necessary for trifluralin residues in processed orange commodities.

---

[4] For the latter case, the samples were placed in a refrigerated room at temperatures ranging from 40 F to 47 F until being processed the following day.

[5] No information is available concerning concentration factors in pulp or molasses. However, considering the hydrophobic nature of trifluralin, it is likely that concentration occurs to the greatest degree in orange oil.

Reference

Decker, O.D., D.D. Shackelford, and D.K. Ervick. 1992. "Determination of Residues of Trifluralin in Oranges and Processed Products Resulting from a Postplant Soil Application of Treflan 5 Herbicide". MRID 426426-01.

cc: S.F., R.F., List A Rereg. Std. File, Circ., DJM.
RDI: ARathman:3/23/93; MMetger:3/29/93; EZager:3/30/93.
EF: 3/30/93.