5-23-94

MEMORANDUM

SUBJECT: **Chlorpyrifos.** Sunflower Seed Processing Study and Sorghum Grain Magnitude of the Residue Study. Reregistration Case No. 0100 Chemical No. 059101 MRID #43181401 and 43191402 DP Barcode D201562 CBRS #13,498

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Tolerances have been established (40 CFR 180.342) for the combined residues of chlorpyrifos and its metabolite 3,5,6-trichloro-2-pyridinol in or on: sunflower seed at 0.25 ppm; sorghum grain at 0.75 ppm; sorghum forage at 1.5 ppm; and sorghum fodder at 6.0 ppm. Tolerances have been also established (40 CFR 186.1000) for the combined residues of chlorpyrifos and its metabolite 3,5,6-trichloro-2-pyridinol in or on sunflower seed hulls at 0.5 ppm and sorghum milling fractions at 1.5 ppm.

The Chlorpyrifos SRR Residue Chemistry Chapter (10/14/88) required data depicting chlorpyrifos residues of concern in/on sunflower seeds harvested 42 days following the last of three foliar applications of chlorpyrifos at 1.5 lb ai/A. The Chlorpyrifos SRR Residue Chemistry Chapter also concluded that residues would not be expected to concentrate in meal, crude oil, refined oil, or soapstock processed from treated seed.

In response, data for sunflower were submitted (MRID #42245906). The data were deemed inadequate because separate residue data for chlorpyrifos in/on sunflower seed and hulls were not provided (L.Cheng, CBRS #9638, 5/19/92). The registrant has provided a new study (MRID #43181401), reviewed below, to address this deficiency.

The Chlorpyrifos SRR also required data depicting chlorpyrifos residues in/on sorghum grain, forage, and fodder harvested 30 days following the last of three foliar treatments of chlorpyrifos at 0.5 lb ai/A and data depicting chlorpyrifos residues in/on sorghum grain harvested 60 days following a foliar application of chlorpyrifos at 1.0 lb ai/A preceded by a foliar application at 0.5 lb ai/A. The tests must be conducted in KS and TX. Appropriate tolerance revisions must be made such that the tolerances for residues in/on sorghum grain,

forage, fodder and milling fractions cover only residues of chlorpyrifos.

In response, data for sorghum grain and fodder were submitted (MRID #42245905). The data were deemed inadequate because no data were presented for forage or milled fractions. Additionally, there was a substantial difference, by an order of magnitude, in the level of chlorpyrifos found in sorghum grain and fodder between the KS and TX trials, even though the same amount of chlorpyrifos was applied and samples were collected with the same PHI (L.Cheng, CBRS #9638, 5/19/92). The registrant has provided a new study (MRID #43181402), reviewed below, to address these deficiencies.

Recommendations

The sunflower processing study is fully acceptable. In the Tolerance Reassessment Chapter of the Reregistration Eligibility Document (RED), tolerances for residues of chlorpyrifos per se in/on sunflower seed should be set at 0.1 ppm. Residue levels in hulls concentrate approximately 2X versus the rac. Therefore, in the RED, tolerances for residues of chlorpyrifos per se in/on sunflower hulls should be revised to 0.2 ppm.

The sorghum magnitude of the residue study for sorghum grain, forage, and fodder is fully acceptable. In the Tolerance Reassessment Chapter of the RED, tolerances for residues of chlorpyrifos per se should be revised as follows: sorghum grain 0.5 ppm; sorghum forage 0.5 ppm; and sorghum fodder 2.0 ppm. Although a sorghum processing study, depicting chlorpyrifos residues in sorghum milled fractions was required by the SRR, residue data are no longer required at this time because sorghum flour in the US is used exclusively as a component for drywall, and not as either a human or animal feed item. The Agency reserves the right to require these data if needed at a later date (D.Edwards and E.Zager, "Updated Livestock Feeds Table for Subdivision O (Residue Chemistry) of the Pesticide Assessment Guidelines", dated 4/28/94).

Conclusions

Sunflower Seed Processing Study (MRID #431841401)

1. CBRS concludes that the test material and test system were adequately described. Geographic representation is adequate because ND accounts for approximately 70% of US sunflower production. Sunflowers were treated with three applications of chlorpyrifos at 1.5 lb ai/A/application for a total application of 4.5 lb ai/A. Plants were treated at 56, 49, and 42 days before harvest.

2. CBRS concludes that the processing procedure was adequately described. Dried sunflower seeds were cleaned using aspiration and screening, then fed to a disc mill to crack the hulls. After cracking, hulls and kernels were separated by aspiration.

3. The analytical method was demonstrated to be adequate for quantitation of chlorpyrifos residues in/on sunflower seed (rac), hulls, and kernels. Representative chromatograms were provided for all samples (controls, fortified controls, and treated samples) as well as standards.

4. Residue levels in the rac, hulls, and kernels were 0.086, 0.148, and 0.048 ppm respectively. Residues levels in hulls concentrate approximately 2X versus the rac. In the Tolerance Reassessment Chapter of the Reregistration Eligibility Document (RED), tolerances for residues of chlorpyrifos per se in/on sunflower seed should be set at 0.1 ppm and at 0.2 ppm for sunflower hulls.

Sorghum Grain, Forage, and Fodder Study (MRID #431841401)

5. CBRS concludes that the test material and test system were adequately described. Geographic representation is adequate. Sorghum grown in KS and TX was treated with either three applications of chlorpyrifos at 0.5 lb ai/A at 44, 37 (36 days for green forage in TX), and 30 days before harvest (Treatment Mode 1) or application of 0.5 lb ai/A followed by 1.0 lb ai/A applied at 67 and 60 days before harvest, respectively (Treatment Mode 2).

6. CBRS concludes that the analytical method used adequately recovers chlorpyrifos residues from sorghum grain, forage, and fodder. Representative chromatograms were provided for all samples (controls, fortified controls, and treated samples) as well as standards.

7. Based on results of this study and the previously reviewed sorghum grain and sorghum fodder magnitude of the residue study (L.Cheng, CBRS #9638, 5/19/92, MRID #42245905), in the Tolerance Reassessment Chapter of the RED, tolerances for residues of chlorpyrifos per se should be revised as follows: sorghum grain 0.5 ppm; sorghum forage 0.5 ppm; and sorghum fodder 2.0 ppm.

8. Although a sorghum processing study, depicting chlorpyrifos residues in sorghum milled fractions was required by the SRR, residue data are longer required at this time because sorghum flour in the US is used exclusively as a component for drywall, and not as either a human or animal feed item. The Agency reserves the right to require these data if needed at a later date (D.Edwards and E.Zager, "Updated Livestock Feeds Table for Subdivision O (Residue Chemistry) of the Pesticide Assessment Guidelines", dated 4/28/94).

Detailed Considerations

Sunflower Seed Processing Study (MRID #431841401)

The purpose of this study was to provide additional residue data on sunflower seeds and hulls to support the reregistration of chlorpyrifos (Lorsban 4E) insecticide for use on sunflowers. Current labels permit up to 3 treatments per season at 1.5 lb ai/A each, with 7 day interval between treatments. Grazing of livestock in treated areas is prohibited.

Test Material

Lorsban 4E, XRM-5003 (lot no. MM920425-376BB), a water emulsifiable formulation of chlorpyrifos was used in this study. This lot was shown to contain 42.8% chlorpyrifos by HPLC analysis (data were referenced, but chromatograms were not provided).

Test System

Sunflowers (Sigco H65A) were grown at Northwood, ND under supervision of Agvise Laboratories. A control plot and treatment plot (40 ft. x 30 ft.) contained approximately 29,200 plants each, with a 30 inch row spacing. The soil was characterized as loam. Adequate climatological data were provided. Seeds were planted on 5/25/93.

The test material was applied to the sunflowers as a broadcast spray (20 gpa). Three applications were made at 1.5 lb ai/A/application for a total application of 4.5 lb ai/A. Plants were treated at 56, 49, and 42 days before harvest (11, 12, and 13 weeks after planting respectively).

3

The entire plot of mature sunflowers (except borders) was harvested on 10/13/93, 42 days after the last treatment. Samples (35 lb of treated and untreated controls) were taken by random grabs from the discharge chute of the combine. Samples were frozen in plastic lined cloth sample bags within 2 hours of collection. Frozen samples were shipped overnight to DowElanco, Indianapolis, ID. On 10/20/93 frozen samples was placed in a shipping box with dry ice and shipped overnight to the processing facility at Texas A&M University. Samples were stored frozen until processing on 11/9/93. After processing, samples (sunflower (rac, unprocessed), clean whole seed, and hulls) were frozen and shipped overnight to DowElanco, Indianapolis, ID, for analysis.

CBRS concludes that the test material and test system were adequately described. Geographic representation is adequate because ND accounts for approximately 70% of US sunflower production.

Processing

Processing was carried out the Food Protein Research and Development Center, Texas A&M University, College Station, TX. An aliquot of the rac was taken before processing occurred. Sunflower seeds (35.3 lb of rac) were first dried to 7-10% moisture in a forced air oven at 130-160 F. Dried seeds (31.4 lb) were cleaned by aspiration to remove light impurities (16.4 g) and then passed over screens sufficient in size to separate whole seed from small and large plant material (638 and 142 g respectively). Cleaned seed (24.2 lb used) was fed through a Bauer disc mill to crack the hulls. After hulls were cracked, hulls (5.8 lb) and kernels (18.4 lb) were separated with a Kice aspirator.

CBRS concludes that the processing procedure was adequately described.

Analytical Method

Frozen samples of the rac, kernels, and hulls were ground and homogenized in liquid nitrogen with an AGVISE Model 2001 hammermill with a 3/16 inch screen. After grinding, the samples were stored frozen at -20 C until analysis. All rac samples were analyzed with 70 days of harvest and processed fractions were analyzed within 59 to 63 days of processing.

Chlorpyrifos residues were determined by DowElanco personnel at the Indianapolis, ID Laboratory using DowElanco Method ACR 90.2, with slight modifications. The limit of detection and validated limit of quantitation were 0.005 and 0.01 ppm respectively.

Chlorpyrifos residues were extracted by shaking samples for 45 min with acetone. An aliquot was removed, concentrated by evaporation, water was added, and the sample partitioned into hexane. The sample was then extracted into acetonitrile and evaporated to dryness. The dried sample was reconstituted in acetone, loaded onto a C_{18} solid phase extraction column, and eluted with MeOH. The eluate was extracted into hexane containing 1% phosphoric acid. This final sample was used for GC analysis.

GC analyses were conducted using an HP 5890 GC with a flame photometric detector (with a phosphorus filter) and a DB-5 capillary column. Sample chromatograms were provided for untreated, treated, and fortified rac, hulls, and seed, as well as standards.

The efficiency of the method was determined at the time of each analysis set by fortifying portions of the control samples with chlorpyrifos and analyzing them as described above. At least one unfortified control and reagent blank were included in each set as well.

Results

Method Recoveries - The analytical method was demonstrated to be adequate for quantitation of chlorpyrifos residues in/on the rac, hulls, and kernels. Results for concurrent recovery samples are summarized in Table 1. Representative chromatograms were provided for all samples (controls, fortified controls, and treated samples) as well as standards.

Table 1. Recovery of chlorpyrifos from fortified control sunflower (rac), hulls, and seed.

Matrix	Fortification Level (ppm)	Number of Samples	Percent Recovery Range
RAC	0.01	6	85.0 - 89.9
	0.10	2	97.8 - 99.2
	0.50	2	79.8 - 82.0
Hulls	0.01	6	81.4 - 100.6
	0.10	2	114.5 - 117.3
	0.50	2	89.9 - 97.1
Kernels	0.01	6	71.9 - 104.8
	0.10	2	92.0 - 96.4
	0.50	2	73.4 - 75.2

Sample Analysis - Results for analysis of the rac, hulls, and kernels are summarized in Table 2. Results for the standard curve used to quantitate residues in each sample were also provided. For all standard curves, the correlation coefficient was $\geq$0.9987.

Residue levels in the rac, hulls, and kernels were 0.086, 0.148, and 0.048 ppm respectively. Residues levels in hulls concentrate approximately 2X versus the rac. In the Tolerance Reassessment Chapter of the Reregistration Eligibility Document (RED), tolerances for residues of chlorpyrifos per se in/on sunflower seed should be set at 0.1 ppm and at 0.2 ppm for sunflower hulls.

Table 2. Results for analysis of the rac, hulls, and seeds. Sunflower plants were treated with three applications of chlorpyrifos at 1.5 lb ai/A/application for a total application of 4.5 lb ai/A. There was a 42 day PHI. Results are the average of duplicate analyses.

Matrix	Chlorpyrifos Found (ppm)
RAC	0.086
Hulls	0.148
Kernels	0.048

Storage Stability

Samples from this study were stored frozen at approximately -20 C for 59 to 70 days before analysis. The Chlorpyrifos SRR noted that chlorpyrifos is stable in plant samples stored at subfreezing temperatures and no additional data are required on this topic.

5

Sorghum Grain, Forage, and Fodder Study (MRID #431841401)

Current Lorsban 4E labels allow for a maximum use rate of 1.5 lb ai/A per growing season. The treated crop is not to be used for grain, forage, fodder, hay or silage within 30 days after application at 0.5 lb ai/A or within 60 days after application using rates above 0.5 lb ai/A.

Test Material

Lorsban 4E insecticide, XRM-5003 (lot no. MM920425-376BB), a water emulsifiable formulation of chlorpyrifos was used in this study. This lot was shown to contain 42.8% chlorpyrifos by HPLC analysis (data were referenced, but chromatograms were not provided).

Test System

The test material was applied (CO_2 backpack sprayer, flat fan nozzle, 18 gal/A) to sorghum in two locations, Elk City, KS, and Idalou, TX, with two different treatment modes. The first treatment mode consisted of three applications at 0.5 lb ai/A applied at 44, 37 (36 days for green forage in TX), and 30 days before harvest. The second treatment mode consisted of applications of 0.5 lb ai/A followed by 1.0 lb ai/A applied at 67 and 60 days before harvest, respectively.

Sorghum (grain sorghum/F200) was planted on 7/18/93 in KS and on 6/2/93 in TX. Samples collected included sorghum grain, forage, and fodder. Forage was sampled by collecting at least 12 plants per plot. Mature grain was collected with a combine. Fodder was collected after combining from at least 12 different areas within the plot. Collected samples were placed into plastic bags and frozen within 3 hours of collection. Weights of samples collected were provided. Samples were shipped frozen to the DowElanco North American Environmental Chemistry Laboratory, Indianapolis, ID, using an overnight service. Samples were stored frozen as bulk field samples until preparation at the laboratory.

Weather data from the field sites, along with 30 year average of the closest NOAA weather stations, were provided. Temperatures at the TX site were within approximately 2 F of the 30 year max/min temperatures. For the KS site, temperatures were within approximately 4 and 9 F of the maximum and minimum 30 year averages respectively. Rainfall was below the 30 year average for all months at both sites with the exception of September at the KS site. Crop distress was noted at the KS site in late August, but the stress had alleviated with rain in September.

CBRS concludes that the test material and test system were adequately described. Geographic representation is adequate.

Analytical Method

Samples were prepared by freezing with liquid nitrogen, breaking some samples by hand after freezing, and grinding through an Agvise Model 2001 hammermill. Chlorpyrifos residues were determined using DowElanco Method ACR 84.4S3. Briefly, residues are extracted from samples with acetone, the extracts are centrifuged, reduced in volume, and cleaned up on a Sep-Pak C18 cartridge and eluted with MeOH. After the MeOH was acidified with dilute phosphoric acid, residues were partitioned to hexane and analyzed using GC/FPD. This

method was discussed in the Chlorpyrifos SRR, where recoveries for a number of various matrices were reported (including sorghum grain, forage, and fodder) and found to be acceptable.

Results

Method Recoveries - The analytical method was demonstrated to be adequate for quantitation of chlorpyrifos residues in/on sorghum grain, forage, and fodder. Results for concurrent recovery samples are summarized in Table 3. Representative chromatograms were provided for all samples (controls, fortified controls, and treated samples) as well as standards. The limit of detection in grain was 0.002 ppm, in forage 0.008 ppm, and in fodder 0.009 ppm.

CBRS concludes that the analytical method used adequately recovers chlorpyrifos residues from sorghum grain, forage, and fodder.

Table 3. Recovery of chlorpyrifos from fortified control sorghum grain, forage, and fodder.

Matrix	Fortification Level (ppm)	Number of Samples	Percent Recovery Range
Grain	0.01	6	71 - 89
	0.05	2	73 - 82
	0.10	2	79 - 86
	0.25	2	76 - 91
	0.50	2	89 - 93
Forage	0.01	6	77 - 91
	0.05	2	78 - 83
	0.10	2	77 - 80
	0.25	1	81
	0.50	2	80 - 87
			Fodder0.01782 - 98
	0.05	1	88
	0.10	2	77 - 80
	0.25	3	79 - 88
	0.50	2	76 - 85
	1.00	2	86 - 87
	2.00	2	82

Sample Analysis - Results for the analysis of sorghum grain, forage, and fodder are presented in Table 4. As in the previously reviewed sorghum magnitude of the residue study (L.Cheng, CBRS #9638, 5/19/92, MRID #422459-05), there was a substantial difference in the level of chlorpyrifos found in sorghum grain and fodder between the KS and TX trials, even though the

same amount of chlorpyrifos was applied and samples were collected with the same PHI. This difference also exists for the sorghum forage results. Results from the KS site are consistently higher than those from the TX site. The results reported in MRID #422459-05 are reproduced below in Table 5 for comparison to the present results.

The registrant suggested that a possible reason for the difference was that sorghum in KS experienced drought stress. Additionally, because sorghum in KS was planted and harvested at a later date than that in TX, it experienced cooler average temperatures. However, crop health was good at both sites at harvest time with no stunting of growth noted.

Based on results of this study and the previously reviewed sorghum grain and sorghum fodder magnitude of the residue study (L.Cheng, CBRS #9638, 5/19/92, MRID #42245905), in the Tolerance Reassessment Chapter of the RED, tolerances for residues of chlorpyrifos per se should be revised as follows: sorghum grain 0.5 ppm; sorghum forage 0.5 ppm; and sorghum fodder 2.0 ppm.

Although a sorghum processing study, depicting chlorpyrifos residues in sorghum milled fractions was required by the SRR, residue data are no longer required at this time because sorghum flour in the US is used exclusively as a component for drywall, and not as either a human or animal feed item. The Agency reserves the right to require these data if needed at a later date (D.Edwards and E.Zager, "Updated Livestock Feeds Table for Subdivision O (Residue Chemistry) of the Pesticide Assessment Guidelines", dated 4/28/94).

Table 4. Results for analysis of sorghum grain, forage, and fodder. Sorghum was treated with either three applications of chlorpyrifos at 0.5 lb ai/A applied at 44, 37 (36 days for green forage in TX), and 30 days before harvest (Treatment Mode 1) or application of 0.5 lb ai/A followed by 1.0 lb ai/A applied at 67 and 60 days before harvest, respectively (Treatment Mode 2). Results are the average of duplicate analyses.

Matrix	Treatment Mode	PHI (days)	Location	Chlorpyrifos Residues Found (ppm)
Grain	1	30	KS	0.199
			TX	0.024
	2	60	KS	0.002
			TX	<0.002
Forage	1	30	KS	0.137
			TX	0.035
	2	60	KS	0.040
			TX	0.009
Fodder	1	30	KS	1.32
			TX	0.168
	2	60	KS	0.342
			TX	0.781

Table 5. Results for analysis of sorghum grain and fodder reported in MRID #422459-05 (reproduced exactly

from L.Cheng memo, CBRS #9638, 5/19/92).

3 x 0.5 lb ai/A or 0.5 + 1.0 lb ai/A PHI (days)	Sorghum Grain (ppm)	Sorghum Fodder (ppm)
29 or 30	0.20 - 0.29 (KS) 0.026 - 0.048 (TX)	0.28 - 0.39 (KS) 0.008 - 0.012 (TX)
60	0.085 - 0.22 (KS) 0.007 - 0.028 (TX)	0.037 - 0.168 (KS) 0.005 - 0.018 (TX)

Storage Stability

Samples from this study were stored frozen at approximately -20 C for 43 to 114 days before analysis. The Chlorpyrifos SRR noted that chlorpyrifos is stable in plant samples stored at subfreezing temperatures and no additional data are required on this topic.

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