5-18-92

MEMORANDUM

SUBJECT: Chlorpyrifos. Case # 0100. ID # 59101. Residue Data in Response to Notice of 9/18/91. MRID # 422459-04, -05, -06 & -07. CBRS # 9638. DP Barcode: D176281.

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In response to chlorpyrifos data call-in, DowElanco has submitted data under guideline # 171-4 (k) for sweet corn, sorghum, sunflowers, and snap bean. Chlorpyrifos is O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate; it is on list A for reregistration.

Product Chemistry and Residue Chemistry chapters were issued 2/29/84; the Guidance document for chlorpyrifos was issued 9/28/84. A Second Round Review (SRR) to the Guidance document was issued 10/14/88. SRR concluded that the parent compound and its metabolite 3,5,6-trichloropyridinol (TCP) are the residues of concern in plants. However in 1988, TOX decided that TCP is not of toxicological concern (memo dated 11/29/88, Alan Levy of TOX II to D. Edwards of RD) and need not be regulated. Consequently, the conclusions stated in the Residue Chemistry chapter of the Chlorpyrifos Second Round Review (SRR) must be revised to delete all data requirements pertaining to TCP (Addendum to the Residue Chemistry chapter, SRR, D. Edwards, 1/13/89).

Current tolerances in 40 CFR 180.342 represent residues of chlorpyrifos and TCP.

1/7

Crop residue data submitted in this package will be reviewed for completeness according to the data requirements reported in the 1/13/89 memo.

Residues of chlorpyrifos were determined by GC with minor modifications (Method ACR 90.2 for sunflower and Method ACR 84.4 for sorghum, sweet corn, and snap bean). When using Method ACR 90.2, chlorpyrifos was extracted from the substrate with acetone. An aliquot of the extract was evaporated, the chlorpyrifos was partitioned into hexane, and then into acetonitrile. The acetonitrile was evaporated off, and the residue was dissolved in aqueous acetone. The sample was cleaned up on an C-18 column eluting with methanol into dilute phosphoric acid. The chlorpyrifos was partitioned into a known volume of hexane. An aliquot of the hexane solution was analyzed by GC using flame photometric detection.

When following Method ACR 84.4, chlorpyrifos was extracted from the substrate with acetone. An aliquot of the extract was evaporated and water was added. The sample was forced through a C-18 column using methanol as the eluant. The methanol was acidified with dilute phosphoric acid (for sorghum grain the methanol was eluted into water while for fodder, the methanol was acidified with dilute phosphoric acid). The chlorpyrifos was then partitioned into a known volume of hexane. A portion of the hexane solution was analyzed by GC using flame photometric detection.

The limit of quantitation was 0.01 ppm in all cases. Except where noted, all field samples after harvest were bagged, frozen and shipped frozen to the Environmental Chemistry Labs of DowElanco in Midland, MI for residue analysis.

Sunflower (MRID # 422459-06)

The 1/13/89 memo stated that "[d]ata depicting chlorpyrifos residues in or on sunflower seeds harvested 42 days following the last of 3 foliar applications of the 4 lb/gal EC formulation 1.5 lb ai/A. The test must be conducted in ND, since this state accounted for ca 70% of the 1985 U.S. sunflower seed production (Agricultural Statistics, 1986, p. 131). Appropriate tolerance revisions must be proposed such that the tolerances for residues in or on sunflower seeds and hulls cover only residues of the parent, chlorpyrifos."

Three applications of LORSBAN 4E were applied to sunflowers in North Dakota at a rate of 1.5 qts/A (1.5 lb ai/A) as a dilute spray. These were made 56, 49, and 42 days before harvest using broadcast spray equipment and a spray volume of 15 gallons per acre. Four sample replicates of sunflowers from a single plot (40' by 130') were randomly collected. The sunflower heads from each replicate were emptied into the combine. Samples were collected from the seed hopper, placed in bags and immediately frozen. The

field samples were milled and subsamples were saved or retained. All samples were stored frozen until analysis. Samples were stored frozen for <5 months before analysis.

Recoveries of 72-92% were obtained when sunflower samples were fortified with 0.01, 0.05, or 0.10 ppm chlorpyrifos. Controls were reported as "0.00 ppm". Residue of chlorpyrifos in sunflowers ranged from 0.024 ppm to 0.051 ppm.

Sorghum (MRID # 422459-05)

"Data depicting chlorpyrifos residues in or on sorghum grain, forage, and fodder harvested 30 days following the last of 3 foliar applications of the 4 lb/gal EC formulation at 0.5 lb ai/A and data depicting chlorpyrifos residues in or on sorghum grain harvested 60 days following a foliar application of the 4 lb gal EC formulation at 1 lb ai/A preceded by a foliar application at 0.5 lb ai/A. The tests must be conducted in KS (26%) and TX (22%), since these states accounted for ca 70% of 1985 U.S. sorghum production, if KS is representative of MO (11%) and NE (14%) (Agricultural Statistics, 1986, 0. 52). Appropriate tolerance revisions must be proposed such that the tolerances for residues in or on sorghum grain, forage, fodder and milling fractions cover only residues of the parent, chlorpyrifos."

LORSBAN 4E was applied to sorghum in KS and TX at 2 different rates. The first application rate consisted of 3 foliar applications at the rate of 0.5 lb ai/A applied 44, 37, and 29 or 30 days before harvest in KS and TX. The second application rate consisted of foliar applications at the rate of 0.5 lb ai/A followed by 1.0 lb ai/A applied 67 and 60 days before harvest, respectively. For application regime one, samples of sorghum grain and fodder were collected 29 and 30 days following the last application at KS and TX, respectively. For application regime two, samples were collected 60 days after the last application. Mature sorghum grain was sampled by hand and thrashed or mechanically thrashed and collected. The fodder was sampled by collecting 12 grabs by hand, or from behind the combine after the sorghum had been cut. The grain and fodder were placed into bags and frozen immediately. All locations had 4 replicate samples. Sorghum grain was processed using a Hobart grinder and the fodder was milled with a 3 mm screen. All samples were stored frozen until analyzed (<2 months).

Recoveries ranged from 67% to 131 % (with an average of 92%) when sorghum grain was fortified with chlorpyrifos at 0.01, 0.05, 0.10, and 0.50 ppm; and ranged from 68% to 116% (with an average of 100%) when sorghum fodder was fortified at 0.01, 0.05, 0.10, and 0.50 ppm chlorpyrifos. Controls contained 0.007 ppm or less chlorpyrifos in grain or $\leq$0.009 ppm in fodder.

3

Chlorpyrifos residues on sorghum grain and fodder from trials conducted in KS and TX are tabulated below.

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)

Sweet corn (MRID # 422459-04)

"Data depicting chlorpyrifos residues in or on sweet corn harvested 35 days following the last of 5 foliar applications of the 4 lb/gal EC formulation at 1.5 lb ai/A. The tests must be conducted in CA (10% of fresh market production), FL (29% fresh market), MN (26% of fresh corn for processing), and WI (25% processing), since these states represent the major areas of U.S. production of sweet corn (Agricultural Statistics, 1986, p. 156). Also, data are required depicting chlorpyrifos residues in or on sweet corn harvested 21 days following the last of 11 foliar applications of the 4 lb/gal EC formulation at 1 lb ai/A in 2 gal/A. The tests must be conducted in FL or GA, since this use is limited to these states. An appropriate tolerance revisions must be proposed such that the tolerances for residues in or on sorghum grain and milling fractions cover only residues of the parent, chlorpyrifos. In addition, a tolerance revision must be proposed for corn grain, in accordance with the conclusions previously set forth under PP#3F2884."

Chlorpyrifos was applied to sweet corn a the rate of 1.5 lb ai/A 5 times at 3-8 day intervals using ground application in CA, FL, GA, MN, and WI. A second treatment rate at the rate of 1.0 lb ai/A, for 11 applications, at 3-6 day intervals was made in FL and GA using aerial application. Untreated control plots were maintained at each location. Samples of corn forage and ears were collected 35 days or 21 days after the last application. Each sample of corn forage was taken from 12-16 plants. The plants were cut either by hand or with a chipping machine, bagged and frozen (except for corn samples from Hollandale, MN which were shipped fresh overnight). The corn ears were collected by hand, bagged and frozen. The samples (except those noted above) were shipped frozen to Midland, MI. Corn ear samples had the husks removed and were prepared with the cobs. Samples were stored frozen until analyzed.

Recoveries ranged from 64-111% (92% average) when corn ears were fortified with chlorpyrifos at 0.01, 0.05 or 0.10 ppm; from77-

114% (average = 91%) when sweet corn forage was fortified at 0.01, 0.05, 0.10, 1.0, or 2.0 ppm chlorpyrifos. Controls were reported as <0.002 ppm (ears) and 0.1 ppm or less (for forage). Levels of chlorpyrifos in ears (with the husks removed, see above) and forage are tabulated below.

Site	Rate (lb ai/A)	PHI (days)	Ears (ppm)	Forage (ppm)
CA	5 x 1.5	35	0.001-0.003	0.088-0.231
FL	5 x 1.5	35	0.000	0.030-0.063
	11 x 1.0	21	0.000	0.044-0.159
GA	5 x 1.5	35	0.005	0.075-1.59
	11 x 1.0	21	0.017	0.095-0.138
MN	5 x 1.5	35	0.000	0.39-0.77
WI	5 x 1.5	35	0.002	0.26-1.72

Snap bean (MRID # 422459-07)

"A tolerance must be proposed and appropriate supporting residue data submitted for residues of chlorpyrifos in or on bean hay. Bean seed must be treated at 1 oz ai/cwt and hay grown from treated seed harvested as soon after planting as it would be suitable for use as livestock feed. Also, the registrant must revise the established tolerance for residues in or on bean forage such that only residues of the parent, chlorpyrifos, are covered, in accordance with conclusions set forth previously under PP#3F2884."

LORSBAN 50-SL (50% active) was applied as a coating to snap bean seeds (Bush Blue Lake #47) in a rotating drum mixer by a hand sprayer. A sample of the snap beans was analyzed prior to treatment and the seeds were found to be free of chlorpyrifos residues. The seeds were treated at a rate of 1.0 oz ai/100 lbs of seeds. A sample of treated seeds was also analyzed in triplicate to determine the concentration of chlorpyrifos on seeds: 474, 469, and 613 ppm with an average of 519 ppm. The treated seeds were sent to Eagle, MI, Fresno, CA, and Geneseo, IL for planting within 42-78 days, and to Burdette, MS for planting 161 days after treatment. One control (untreated) plot was also maintained at each planting site.

5

Samples of treated snap bean hay were collected ≈ 70 days after planting. For both the control and treated plots the samples were harvested by snipping the plant at the base of the plant with sheers. The samples were allowed to dry for about 5 days in the field or a greenhouse.

Recoveries ranged from 69-104% (85% average) when snap bean hay was fortified with chlorpyrifos at 0.01, 0.05 or 0.10 ppm. Controls contained <0.008 ppm chlorpyrifos.

Levels of chlorpyrifos in snap bean hay ranged from ≤0.001 ppm to 0.071 ppm when sampled 63, 70, or 83 days after planting.

Storage stability

According to the Residue Chemistry chapter of 1/25/84, chlorpyrifos (or TCP) was found to be stable in samples of apple for up to 4.2 years, and field corn (green forage, fodder and grain), sorghum, and alfalfa (green forage and hay) for 1-27 months, all at -18° C.

CONCLUSIONS AND RECOMMENDATION

1. The information does not satisfy the residue data requirement on sunflowers. Separate residue level of chlorpyrifos in or on sunflower seed and hull are required. The registrant needs to provide chlorpyrifos levels in sunflower seed and hulls separately. Submitted chromatograms of chlorpyrifos standard, a control, fortified sunflower control, and treated sample are adequate.

2. We notice 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 LORSBAN was applied and samples were collected the same number of days after the last treatment. The registrant needs to explain the observed difference in chlorpyrifos level. Residue data in milled fractions are also required but have not been provided. Copies of chromatograms representing chlorpyrifos standard, controls of sorghum grain and fodder, and chlorpyrifos fortified samples, and treated samples are acceptable.

3. From the field data sheets, corn field samples were stored frozen <6 months. The current tolerance levels are 0.1 ppm for sweet K-CWHR and 10 ppm for forage and fodder. The submitted residue data show 0.017 ppm max chlorpyrifos in ears minus husks and 1.72 ppm max chlorpyrifos in forage.

According to the 1/13/89 memo, corn processing data are also required. These data remain outstanding.

6

4. Stored samples of snap bean hay were analyzed within 6 months (from the field data sheets). Residues of chlorpyrifos per se in bean hay were up to 0.071 ppm.

5. The registrant should propose tolerances in terms of chlorpyrifos per se (only) for sweet corn (K+CWHR), sweet corn forage, and snap bean hay. Tolerance revisions to reflect residues of only the parent compound will be required when adequate residue data for sunflowers, sorghum, and corn processed commodities are available to determine appropriate tolerance levels.

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7