

MEMORANDUM

SUBJECT: **Chlorpyrifos.** Magnitude of the Residue in Onions and Corn Processed Commodities. Reregistration Case No. 0100. Chemical No. 059101. MRIDs #42649001 and 42649002. DP Barcode D188151. CBRs #11,372.

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THRU: Edward Zager, Chief
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TO: Joanne Edwards, PM Team 73
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The Chlorpyrifos 1988 SRR Residue Chemistry Chapter concluded that no data are available reflecting use of the chlorpyrifos G MAI formulations on onions and no data are available depicting residues in all fractions from wet and dry milling and grain dust from corn grain bearing measurable weathered residues.

DowElanco has submitted data for corn processing (1993; MRID 4264902) and onion residue data (1983; MRID 42649001). These data have been reviewed by Acurex and have undergone secondary review in CBRs to reflect Branch policies.

The submitted data indicate that chlorpyrifos residues in or on green or bulb onions are not likely to exceed the established tolerance (0.5 ppm) for onions (bulb) following a single soil application of chlorpyrifos at 1.0 lb ai/A. However, these data do not provide adequate geographic representation (all trials were conducted in MI). Additional data are required from tests conducted in ID or OR and NY.

The product label for the 15% G formulation is not clear with respect to geographical restrictions for the use on onions. This and other pertinent product labels must be revised to state restrictions clearly.

The corn grain processing study is fully adequate, no additional data are required. In a Chlorpyrifos Final Rule dated 4/1/93 (D.Barolo), tolerances for chlorpyrifos *per se* at 0.05 ppm are established for residues in or on field corn grain (180.342[c]); however, the food additive tolerance in or on corn oil and the feed additive tolerance in or on corn soapstock (at 3.0 ppm and 1.0 ppm respectively) are expressed in terms of combined residues of chlorpyrifos and its TCP metabolite (40 CFR 185.1000[a] and 40 CFR 186.1000[a]).

The data indicate that food/feed additive tolerances for residues of chlorpyrifos per se of 0.1 ppm are required in or on corn grain milled fractions (grits, meal, and flour), based on concentration factors ranging from 1.25x in grits to 2x in flour. A food additive tolerance for residues of chlorpyrifos per se in or on corn oil at 0.25 ppm is required, based on the highest observed concentration factor of 4.5x. A feed additive tolerance for residues of chlorpyrifos per se is required in or on grain dust at 0.5 ppm, based on a concentration factor of approximately 10x in the <420 μ dust fraction.

Amendments to 40 CFR 185.1000 and 186.1000 should be made to reflect the above noted tolerances required for residues of chlorpyrifos per se in or on corn processed commodities.

If you need additional input please advise.

Attachmnet.

cc: S.F., circ., R.F., List B File, S.Knizner, ACUREX
H7509C:CBRS:CM#2:305-6903:SAK:sak:Chlorpyr.oni:8/18/93

CHLORPYRIFOS
(Chemical Code 059101)
(CBRS No. 11372; DP Barcode D188151)

TASK 3

**Registrant's Response
to Residue Chemistry Data
Requirements**

April 22, 1993

Contract No. 68-DO-0142

Submitted to:

U.S. Environmental Protection Agency
Arlington, VA 22202

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CHLORPYRIFOS

(Chemical Code 059101)

(CBRS No. 11372; DP Barcode D188151)

REGISTRANTS RESPONSE TO RESIDUE CHEMISTRY DATA REQUIREMENTS

Task-3

BACKGROUND

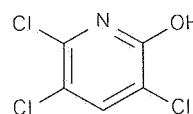
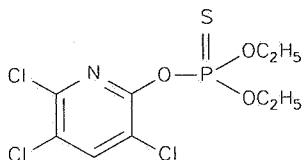
The Chlorpyrifos 1988 SRR Residue Chemistry Chapter concluded that no data are available reflecting use of the G MAI formulations on onions and no data are available depicting residues in all fractions from wet and dry milling and grain dust from corn grain bearing measurable weathered residues.

The current DowElanco submissions contain corn processing (1993; MRID 4264902) and onion residue data (1983; MRID 42649001). The Conclusions and Recommendations stated below apply only to residues in onion and corn processed fractions.

The nature of the residue in plants is adequately understood. Currently, tolerances for chlorpyrifos residues in or on some plant commodities are expressed in terms of the combined residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol (TCP) (40 CFR §180.342[a] and [b]; 40 CFR §185.1000[a] and §186.1000[a]). Tolerances for residues in or other plant commodities and in animal commodities are expressed in terms of chlorpyrifos per se (40 CFR §180.342[c]). A Toxicology Branch memorandum (A. Levy, dated 12/15/88) presented data indicating that TCP is less toxic than chlorpyrifos and is not a cholinesterase inhibitor; it stated that Tox Branch had no objection to removing TCP from the Tolerance expression.

The Pesticide Tolerances and Food Additive Regulations for Chlorpyrifos Final Rule (D.Barolo, 4/1/93) states that "...Agency has concluded that the TCP metabolite is not of toxicological concern." The Rule modified 40 CFR 180.342 by moving many, **but not all**, racs from 180.342[a] to 180.342[c]. In the Final Rule, tolerances for chlorpyrifos per se at 0.05 ppm are established for residues in or on field corn grain (180.342[c]); however the tolerance for onions, dry bulb, at 0.5 ppm is still expressed in terms of combined residues of chlorpyrifos and its TCP metabolite (180.342[a]).

The food additive tolerance in or on corn oil and the feed additive tolerance in or on corn soapstock (at 3.0 ppm and 1.0 ppm respectively) are expressed in terms of combined residues of chlorpyrifos and its TCP metabolite (40 CFR 185.1000[a] and 40 CFR 186.1000[a]).



Chlorpyrifos

TCP

Adequate methodology is available for enforcing tolerances for residues of chlorpyrifos. The available methodology is described in the Chlorpyrifos Second Round Review of 11/89. That review noted that a considerable proportion of the TCP residue was released by base hydrolysis; therefore, it concluded that methodology should be developed to include a base hydrolysis step. However, as the tolerance definition is to be revised to remove TCP, new methodology is not needed.

A Codex MRL (CXL) of 0.05 ppm has been established for residues of chlorpyrifos in or on bulb onions. This is one tenth the current established U.S. tolerance for bulb onions. After the additional data required for onions has been reviewed and accepted, a determination will be made as to whether or not the registered use pattern will permit decreasing the U.S. tolerance to achieve compatibility with the Codex MRL. As the metabolite TCP will in all likelihood be removed from all tolerance definitions, differences in tolerance expression should not present an obstacle to compatibility. There is no Codex MRL for chlorpyrifos in or on field corn grain.

CONCLUSIONS/RECOMMENDATIONS

- 1.a. The submitted data indicate that chlorpyrifos residues in or on green or bulb onions are not likely to exceed the established tolerance (0.5 ppm) for onions (bulb) following a single soil application of chlorpyrifos at 1.0 lb ai/A. However, these data do not provide adequate geographic representation (all trials were conducted in MI). Additional data are required from tests conducted in ID or OR and NY.
- 1.b. The product label for the 15% G formulation is not clear with respect to geographical restrictions for the use on onions. This and other pertinent product labels must be revised to state restrictions clearly.
2. The corn grain processing study is adequate.
- 2.a. The data indicate that food/feed additive tolerances for residues of chlorpyrifos per se of 0.1 ppm are required in or on corn grain milled fractions (grits, meal, and flour), based on concentration factors ranging from 1.25x in grits to 2x in flour.
- 2.b. A food additive tolerance for residues of chlorpyrifos per se in or on corn oil at 0.25 ppm is required, based on the highest observed concentration factor of 4.5x.
- 2.c. A feed additive tolerance for residues of chlorpyrifos per se is required in or on grain dust at 0.5 ppm, based on a concentration factor of approximately 10x in the <420 μ dust fraction.

- 2.d. Amendments to 40 CFR 185.1000 and 186.1000 should be made to reflect the above noted tolerances required for residues of chlorpyrifos per se in or on corn processed commodities.

DETAILED CONSIDERATIONS

Residue Analytical Methods

DowElanco (1983; MRID 42649001, and 1993; MRID 42649002) submitted method descriptions along with residue data on onions and field corn. Chlorpyrifos and TCP residues in or on onions were determined using modifications to methods ACR 72.15 and ACR 71.19R. Chlorpyrifos residues in corn and corn processed fractions (except oil) were determined using method ACR 84.4.S3. Chlorpyrifos residues in processed corn oils (crude and refined) were determined using a modification to method ACR 90.2.

Chlorpyrifos residues are extracted from onions into MeOH. The MeOH extract is concentrated, dissolved in water, the residues are partitioned into hexane, and then determined by GC/NPD. The detection limit is 0.05 ppm.

TCP residues are extracted from onions into MeOH. Residues in the MeOH extract (acidified with HCl and NaCl solution added) are then partitioned into benzene. The benzene solution is cleaned up on an acidic alumina column (eluted into diethyl ether). Residues are then partitioned into 0.25M sodium bicarbonate solution. The solution is then acidified (HCl) and partitioned with benzene. The benzene solution is dried over sodium sulfate, BSA is added, and the solution is concentrated for analysis. TCP residues are determined by GC/ECD. The detection limit is 0.05 ppm.

Chlorpyrifos residues are extracted from corn and corn processed fractions (except oil) into acetone. For dry milled dust, the acetone is analyzed by GC/FPD without further cleanup. For all other milled fractions (except oil), the acetone extract is concentrated, dissolved in water, applied to a C₁₈ SPE column, and the residues are eluted with MeOH. The MeOH is acidified with dilute phosphoric acid, the residues are partitioned into hexane, and then determined by GC/FPD. The detection limit is 0.01 ppm.

Chlorpyrifos residues are extracted from corn oil into hexane, partitioned into acetonitrile, concentrated, dissolved in water, applied to a C₁₈ SPE column, and then the residues are eluted with MeOH. The MeOH is acidified with dilute phosphoric acid, the residues are partitioned into hexane, and then determined by GC/FPD. The detection limit is 0.01 ppm.

Recoveries determined concurrently with residue samples are summarized below in the discussions of "Magnitude of the Residue."

Storage Stability

The 1984 Chapter discusses storage stability data on field corn and onions. Recoveries of parent and TCP from field corn fortified and stored frozen 0 °C for 1-27 months were 65-110%. Recoveries of parent and TCP from onions fortified and stored frozen -20 °C for 1-23 months were 72-123%. The available storage stability data are adequate to validate the submitted studies on onions and corn.

Magnitude of the Residue

Onions. A tolerance of 0.5 ppm has been established for the combined residues of chlorpyrifos and its metabolite TCP in or on dry bulb onions (40 CFR §180.342[a]). The 0.5, 1, and 15% G formulations (EPA Reg. Nos. 62719-14, -34, -210) and two EC formulations (EPA Reg. Nos. 62719-23 and -56) are currently registered. The 15% G label specifies a single in-furrow application at 1 lb ai/A (given an 18-inch row spacing). Specific timing of application (or PHI) was not specified.

The SRR indicated that the 4 lb/gal EC formulation is registered for soil drench application made at seeding at 0.03 lb ai/1,000 ft of row (approximately 1 lb ai/A); this use is restricted to ID, MI, MN, NJ, NY, OH, OR, WA, and WI. No PHI is listed for onions. The 4 lb/gal EC is registered in MI for direct spray application to the base of seedlings or transplants at 1 lb ai/A (EPA SLN No. MI850006). No PHI is listed.

DowElanco (1983; MRID 42649001) submitted data generated by IR-4 Central Region Analytical Laboratory at Michigan State University depicting chlorpyrifos residues in or on green and dry bulb onions from 3 tests conducted in MI. Green onions were harvested 83 days following an at-seeding (soil application) with the 15% G at 1 lb ai/A (1x). Dry bulb onions were harvested 53 days following two applications at transplanting, one band soil application of the 15% G (EPA Reg. No. 464-523) and one foliar (directed spray) application of the 4 lb/gal EC (EPA Reg. No. 464-448) at 1 lb ai/A each (2x). Dry bulb onions were also harvested 54 days following three applications, one band soil application of the 15% G (EPA Reg. No. 464-523), and two foliar (directed spray) applications of the 4 lb/gal EC (EPA Reg. No. 464-448) at 1 lb ai/A each (3x).

Samples were stored for up to 280 days prior to extraction and analysis. Chlorpyrifos and TCP residues in or on green and bulb onions were determined using the methods described in the residue analytical methods section above. Recoveries of chlorpyrifos were 107% from green and bulb onions fortified at 0.1 ppm.

Chlorpyrifos and TCP residues were, respectively, <0.05-0.08 ppm and <0.05 ppm in or on three treated green onion samples harvested 83 days following at seeding (soil application) at 1x the maximum recommended rate. Apparent residues of chlorpyrifos and TCP were nondetectable (<0.05 ppm) in or on three control samples of green onions.

Chlorpyrifos and TCP residues were <0.05-0.085 ppm in or on three treated bulb onion samples harvested 53 days following two applications (one soil application, and one directed spray application) at 1 lb ai/A each (2x the maximum recommended rate). Apparent residues of chlorpyrifos and TCP were nondetectable (<0.05 ppm) in or on three control samples of bulb onions.

Chlorpyrifos and TCP residues were <0.05 ppm in or on three treated bulb onion samples harvested 54 days following three applications (one soil application, and two directed spray application) at 1 lb ai/A each (3x the maximum recommended rate). Apparent residues of chlorpyrifos and TCP were nondetectable (<0.05 ppm) in or on three control samples of bulb onions.

Geographic representation is not adequate for the G formulation. The test state MI accounted for approximately 9% of the U.S. storage onion production in 1990 (Agricultural Statistics, 1990, p. 157). Additional data are required from tests conducted in ID or OR and NY.

The product label for the 15% G formulation is not clear with respect to geographical restrictions for the use on onions. This and other pertinent product labels must be revised to state restrictions clearly.

The tests conducted in MI are adequate to represent the 4 lb/gal EC (EPA SLN No. MI850006) use which is registered for direct spray application to the base of seedlings or transplants at 1 lb ai/A.

Processed Food/Feed

Corn Processed Commodities. A tolerance of 0.05 ppm in or on field corn (40 CFR §180.342[c]) is established for chlorpyrifos per se. Tolerances of 3.0 ppm in corn oil (40 CFR §185.1000[a]), and 1.0 ppm in corn soapstock (40 CFR §186.1000[a]) have been established for the combined residues of chlorpyrifos and its metabolite TCP. A REFS search dated 4/16/93 indicated that the 7.5, and 15% G formulations (EPA Reg. Nos. 62719-85, and -34), two EC formulations (EPA Reg. Nos. 62719-23 and -56), and one WP formulation (EPA Reg. Nos. 62719-38) are currently registered for use on field corn. The 1988 SRR provides a summary of the current uses.

DowElanco (1993; MRID 42649002) submitted data depicting chlorpyrifos residues in or on corn grain and "dust" (screenings) and in processed corn commodities. In two tests conducted in IL and MI, chlorpyrifos (4 lb/gal EC) was applied at 7.5 lb ai/A (7.5x the maximum label rate) in five ground applications. Control and treated plots were harvested 35 days posttreatment. The sample storage interval from harvest to analysis was approximately 23 months; samples were stored frozen. Using commercially simulated practices, corn grain was dry-milled to yield screenings of varying sizes, grits, meal, flour, and crude and refined oil, and wet-milled to yield starch, gluten, and crude and refined oil. Processing was conducted at the Food Protein Research and Development Center, Texas A&M University. Residue analyses were conducted by DowElanco.

Control and treated samples of corn grain and dust and each processed commodity were analyzed for chlorpyrifos residues using the methods described in the residue analytical methods section above. Recoveries were 88% from grain, 82% from grits, meal, and flour, 94% from starch, and 71% from oil; samples were fortified at 0.01-1 ppm. Apparent residues of chlorpyrifos in or on control samples (IL) of grain and in each of the processed commodities (except screenings) were nondetectable (<0.01 ppm) (reported 0.000-0.003 ppm). Apparent residues of chlorpyrifos in or on control screening samples (6) were reportedly 0.000-0.024 ppm. Chlorpyrifos residues were nondetectable (<0.01 ppm) in or on grain harvested from corn in the IL test treated with chlorpyrifos at 7.5 lb ai/A (7.5x). Detectable residues were found in oil (0.01-0.02 ppm) and screenings (up to 0.37 ppm).

RAC grain samples from the MI test bore detectable residues of 0.04 ppm. Therefore, the results of this test (presented in Tables 1 and 2) were used to assess the potential for residue concentration. Residues were present in the control grain samples at 0.016 ppm and concentrated in the control fractions processed from the control grain. The report indicated that these were actual chlorpyrifos residues rather than apparent residues from interfering substances.

Table 1. Chlorpyrifos residues in corn grain (from the MI) test and processed fractions.

Fraction	Chlorpyrifos residues (ppm) ^a		Concentration Factor
	Control	Treated	
Grain	0.016	0.04	Not applicable
(Dry milled fractions)			
Grits (large)	0.003	0.02	--
(Medium)	0.004	0.03	--
(Small)	0.005	0.05	1.25
Meal	0.011 0.009 0.011	0.06	1.5
(Coarse)	0.006	0.06	1.5
Flour	0.013 0.014 0.013	0.08	2
Oil (Crude)	0.029	0.08	2
(Refined)	0.022	0.08	2
(Wet milled fractions)			
Coarse gluten starch	0.006 0.006 0.006 0.007	0.07	1.7
Starch	0.000	0.002	--
Oil (crude)	0.032	0.17	4.25
(refined)	0.043	0.18	4.5

^aResidues in treated samples are corrected for concurrent method recoveries of 88% for grain, 82% for grits, meal, and flour, 94% for starch, and 71% for oil.

Table 2. Concentration of chlorpyrifos residues in grain dust fractions from corn grain.

Fraction	Chlorpyrifos residues (ppm)		Concentration Factor
	Control	Treated	
Grain	0.016	0.04	Not applicable
Dust (2030 μ)	0.071	0.157 (0.086)	2.2
(1190 μ)	0.151	0.249 (0.098)	2.5
(841 μ)	0.143	0.293 (0.150)	3.8
(420 μ)	0.235	0.341	8.5
	0.022	0.334	8.4
	0.211	0.318	8.0
			(average 8.3)
(< 420 μ)	2.24 ^a	0.493	12.3
	0.822	0.369	9.2
	0.517	0.352	8.8
	0.622		(average 10.3)

^aThe registrant reported that this sample was shown by the Q test to be an outlier.

The corn grain processing study is adequate.

The data indicate that food/feed additive tolerances for residues of chlorpyrifos per se of 0.1 ppm are required in or on corn grain milled fractions, based on concentration factors ranging from 1.25x in grits to 2x in flour.

A food additive tolerance for residues of chlorpyrifos per se in or on corn oil at 0.25 ppm is required, based on the highest observed concentration factor of 4.5x.

A feed additive tolerance for residues of chlorpyrifos per se is required in or on grain dust at 0.5 ppm, based on a concentration factor of approximately 10x in the < 420 μ dust fraction.

References

Citation for the MRID documents and Agency correspondence referred to this review are presented below. The submission reviewed in this document is indicated in shade type.

42649001 Leavitt, R.; Markle, G.; Wells, A. (1983) Chlorpyrifos: Magnitude of Residue on Onions (Green and Bulb) Michigan: Lab Project Number: 452: 5186. Unpublished study prepared by Michigan State University, IR-4 North Central Region Analytical Lab. 30 p.

42649002 Robb, C.; Schotts, B.; Ostrander, J. (1993) Determination of Residues of Chlorpyrifos in Processed Fractions of Corn: Lab Project Number: 90030. Unpublished study prepared by DowElanco and Texas A&M University. 212 p.

Agency Memoranda

CB: None
Subject: Chlorpyrifos Reregistration Standard - Revision to exlude TCP metabolite from existing tolerances; Identifying No. 3F2884; Record No. 233507; HED Project No. 9-0196; Caswell No. 219AA.

From: A. Levy
To: D. Edwards
Date: December 15, 1988
MRID(s): None

CBTS: None
Subject: Meeting to discuss removal of Trichloropyridinol (TCP) from tolerance expression for chlorpyrifos.

From: S. Bacchus
To: CBTS Files
Date: March 22, 1991
MRID(s): None