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PP #3F1306. Chlorpyrifos in various commodities. Comments on amendments of May 21 and August 3, 1973.

Coordination Branch
and Toxicology Branch, RD

Dow Chemical Company now proposed tolerances for combined residues of the insecticide chlorpyrifos [0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate], and its metabolite 3,5,6-trichloro-2-pyridinol as follows:

- 1.5 ppm in or on fat and (on fat basis) in or on meat and meat by-products of cattle;
- 0.2 ppm in or on meat, fat, and meat by-products of turkeys;
- 0.1 ppm (negligible residue) in or on field corn (grain, green forage, and fodder); and
- 0.05 ppm (negligible residue) in or on peaches.

In our review of March 1, 1973, we recommended against the initial proposals. The previous deficiencies are listed below and followed by our comments on the amended data.

Deficiency 1: Storage stability data on crops and animal substrate are needed. In addition, we need to know the lapse of time between sampling and analyses.

Comments: Samples of field corn (green forage, fodder and grain); peaches; bananas (whole, peel and pulp); meat (muscle, liver, kidney, and fat); and milk, fortified with chlorpyrifos at various levels (0.01-5 ppm) and analyzed at intervals up to 49 months afterward show recoveries of about 75% or better. Thus, we conclude that chlorpyrifos is stable under normal frozen storage conditions.

Deficiency 2: Because of the likelihood of incidental residues occurring in peaches from drift, etc., the preharvest interval for peaches should be changed from 14 days to 30 days for a tolerance of 0.05 ppm.

Comments: The petitioner states that the residue studies in the petition were conducted under field conditions. Thus the likelihood of incidental residues occurring in peaches from drift or other cause has already been taken into account. Residue data in the petition show all values for the parent and TCP to be <0.01 and <0.02 ppm, respectively from the proposed use at the recommended 14-day PHI. Therefore, we now conclude that the proposed 0.05 ppm tolerance is appropriate for the recommended use.

Deficiency 3a: Because of variable controls (<0.01-0.08 ppm) for 3,4,6-trichloro-2-pyridinol (TCP) in field corn (forage and fodder), a tolerance of 0.05 ppm is inadequate for combined residues of the parent and TCP. A tolerance of 0.1 ppm is more appropriate for combined residues in field corn (grain, green forage, and fodder).

Comments: The petitioner concurs that a 0.1 ppm tolerance is more appropriate. Section F has been revised to reflect this change.

Deficiency 3b: The question of whether the alkaline hydrolysis step frees the aglycone or whether enzyme hydrolysis is necessary to determine possible plant conjugates of TCP must be resolved to determine the adequacy of the analytical method proposed for corn.

Comments: This question arose because typical phenols normally form conjugates in plants, and because the analytical method for TCP in corn included an alkaline hydrolysis step. It was assumed that the hydrolysis step was incorporated to liberate any possible plant conjugates.

The petitioner points out in this amendment that the alkaline hydrolysis step of the procedure was incorporated to free any adsorbed residues (physically bound) of TCP rather than chemically bound residues. It is further stated that analyses on certain corn substrates which were fortified and extracted one day or more later show more consistent and higher recoveries than when the hydrolysis step was omitted. This same phenomenon was noted in the soil; in this instance, TCP residue was attributed to being physically bound (adsorbed). In addition, it is pointed out that the chemistry of the hydroxypyridines is somewhat different from the typical phenol.

While this information is helpful, it does not alleviate our concern for possible conjugates of 3,5,6-trichloro-2-pyridinol in the corn plant. Therefore, the question of whether the alkaline hydrolysis step frees the aglycone or whether enzyme hydrolysis is necessary to determine possible plant conjugates of TCP still needs to be resolved before we can determine the adequacy of the analytical method proposed for corn.

Deficiency 3c: The pH of the soil in which the corn was grown is needed.

Comments: The petitioner states that the pH of the soil was approximately 6.0 at all test locations. Test locations were: York, Nebraska; Humbolt, Illinois; Sycamore, Ohio; and Scandia, Kansas. Uptake studies show that at a pH of 6, very little residues are translocated in the plant. Information (10/15/73) from the University of Maryland Soil Service Division indicates that a pH of 6.5 is about the optimum for growing corn. Considering this information, we believe that the studies reflect the conditions under which corn is grown. Our question regarding the pH of the soil is resolved.

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Deficiency 4: A 1 part per million tolerance is inadequate for combined residues of chlorpyrifos and TCP in or on fat and (on fat basis) in or on ment and meat byproducts of cattle. A 1.5 part per million tolerance is more appropriate. Alternatively, a 21-day preslaughter interval is needed.

Comments: The petitioner agrees that a 1.5 ppm would be more appropriate. Section F has been revised to reflect this change.

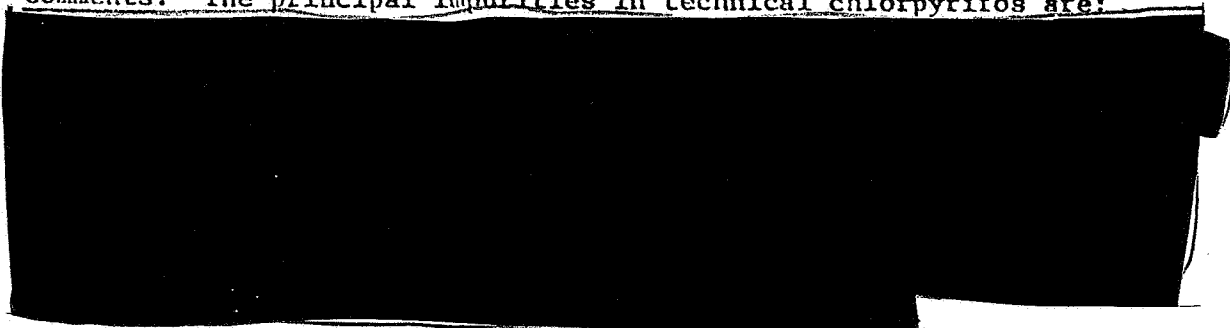
Deficiency 5a: No data are presented to show whether residues are likely to occur in milk from dairy cattle that were treated topically while not lactating. Therefore, the label statement permitting topical treatments of "non-lactating" dairy cattle should be deleted, i.e., the use should be limited to beef cattle only.

b. Alternatively, residue data are needed to show whether residues will result in milk from lactating dairy cattle that were treated topically while dry. If so, an appropriate tolerance in milk and the following label statement are needed: "Should the dairy cow freshen during medication, or if medication has not been withdrawn the required ___ days prior to freshening, milk must not be used for food for ___ days after last treatment." (Insert the appropriate number of days in the blank spaces, provided there is supportive data covering the uses.)

Comments: A revised label is submitted which now limits the use of Dursban 24E to beef cattle only. In addition, the "ear tick" treatment has been removed from the label because of the lack of efficacy data (see petitioner's letter of May 21, 1973, to Ms. P. Critchlow of Standards Branch). Thus, Category 3 of Sec. 180.6(c) applies with respect to residues in milk.

Deficiency 6: The specific identity and amounts of the various impurities in the technical product, particularly the "other chlorinated pyridyl O,O-diethylphosphorothioates" are needed.

Comments: The principal impurities in technical chlorpyrifos are:



IDENTITY OF PRODUCT IMPURITIES NOT INCLUDED

Deficiency 7: Chlorpyrifos and more specifically its hydrolysis product TCP show a tendency to persist in soil. Therefore, residue data on rotated crops are needed before a conclusion can be made regarding residues in followup crops.

Comments: No new data are presented in regard to the above request. The petitioner contends that adequate data are available to show that chlorpyrifos and TCP will not persist in soil. These data were discussed in our review of March 1, 1973. Illinois studies showed ^{that} residues of parent and TCP dissipate in about 4 months. Nebraska studies showed that after one year residues of the parent were about 90% or more dissipated; however, residues of the hydrolysis product, TCP, were present in the top 6 inches of soil at levels up to 2.0 ppm. This is equivalent to about 40-100% of the amount present at zero to 30 days after treatment.


The petitioner speculates that the difference in persistence in the Illinois and Nebraska studies may have resulted because the Illinois plots were fall plowed, thereby diluting the treated soil; whereas, the Nebraska plots were not. In addition, the petitioner alludes to the metabolism studies showing little translocation by plant as further evidence that followup crops will not contain residues.

Dr. Grant N. Smith, Basic Studies on Dursban Insecticide, Down to Earth, 22 (2):3-7 (1966), made the following statement in reference to chlorpyrifos, "The major chemical reaction is a slow hydrolysis of the compound to give the 3,5,6-trichloro-2-pyridinol. In water solutions, soil, etc., the hydrolysis rate has a half-life of about 80-100 days. This means that the compound will be very persistent in the soil and in other situations in which volatility does not play a major role." (Ref. #29, Vol. XII of petition).

It is possible that the plowing may have had some effect on residues in the Illinois study; however, this is not documented. We defer to EEB on the need for crop rotational restrictions.

Addendum to Methodology

In our review of March 1, 1973, we stated that no final conclusion could be made about the adequacy of the methods until the methods were tested in our laboratory. The method trials have been completed and are summarized in our comments of July 9, 1973. The methods were tested on peaches and beef fat. They were considered adequate for determining the parent and inadequate for determining the 3,5,6-trichloro-2-pyridinol. The petitioner stated in a conference on July 31, 1973, that an error was made in the submission of the method for TCP in peaches and beef fat.



The amendment of August 3, 1973, contains the corrected procedure for TCP in fat and peaches. In both procedures (ACR 70.19 for fat, and ACR 71.11 for peaches) a step was inadvertently omitted from the cleanup technique.

In both cases the omitted directions involve washing the alumina cleanup column with a small aliquot of methanol prior to elution of the TCP. The amended procedures are designated 70.19R and 71.11R for beef tissues and peaches, respectively. The petitioner shows adequate validation data for beef tissues (avg. 84% at 0.05-0.5 ppm levels) and peaches (avg. 93% at 0.05-0.5 ppm levels) by these methods.

The petitioner mentioned at the above conference that the residue data for TCP were determined by the correct procedures. Thus, we are not questioning the validity of the residue data in the petition.

The Analytical Methods Section has now tested the amended TCP procedure for beef fat. The amended method for TCP in peaches was not tested because a successful tryout of the same procedure was made on bananas in connection with PP #3F1370. Duplicate recoveries from beef fat were 86% and 79% at a fortification level of 0.1 ppm and 78% and 76% at 0.5 ppm. Controls were <0.005 ppm. Duplicate recoveries from bananas were 88% and 94% at a fortification level of 0.05 ppm and 91% and 98% at 0.1 ppm. Controls were <0.005 ppm. We now conclude that the methods are adequate for determining residues of free TCP. We estimate the sensitivity to be 0.02 ppm for the commodities in this petition.

Conclusions

- 1a. The results of the method trials show that the methods are adequate for the parent and the free metabolite 3,5,6-trichloro-2-pyridinol in plant and animal tissues.
- b. The question of whether the alkaline hydrolysis step frees the aglycone or whether enzyme hydrolysis is necessary to determine possible plant conjugates of TCP still needs to be resolved before we can determine the complete adequacy of the analytical method proposed for corn.
2. Chlorpyrifos is stable under normal frozen storage conditions.
3. The 0.05 ppm tolerance is appropriate for combined residues of the parent and 3,5,6-trichloro-2-pyridinol in peaches from the proposed use.
4. The amended tolerance level of 0.1 ppm is appropriate for combined residues of the parent and free TCP in field corn (grain, green forage, and fodder). The question of whether conjugates are a problem is contingent on the resolution of Conclusion 1b.

5. The amended tolerance level of 1.5 ppm is appropriate for combined residues of chlorpyrifos and TCP in or on fat, and (on fat basis) in or on meat and meat byproducts of cattle from the topical use.

Recommendations

Pharmacological considerations permitting, we recommend for tolerances for combined residues of chlorpyrifos [0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl)phosphorothioate], and its metabolite 3,5,6-trichloro-2-pyridinol as follows:

1.5 ppm in or on fat and (on fat basis) in or on meat and meat byproducts of cattle;

0.2 ppm in on meat, fat, and meat byproducts of turkeys;

0.05 ppm (negligible residue) in or on peaches.

We recommend against the proposed tolerance for field corn (grain, green forage and fodder) because of Conclusion 1b. For further consideration of the corn tolerance, the petitioner should resolve this deficiency.

Data indicate that chlorpyrifos hydrolysis product, TCP, will persist in soil. We defer to the Ecological Effects Branch on the need for crop rotation restrictions.

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FDRGee:cy:10/31/73
RD/I - RSQuick:10/16/73
DVRreed:10/29/73

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