MEMORANDUM

SUBJECT: PP#2F2684/2H5352 and Amendment of July 9, 1982.
Chlorpyrifos in or on sugar beets.
Evaluation of residue data and analytical methodol-
ogy.

FROM: Jesse E. Mayes, Chemist
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TO: Jay S. Ellenberger, PM 12
Registration Division (TS-767)
and
Toxicology Branch
Hazard Evaluation Division (TS-769)

THRU: Charles S. Trichilo, Chief
Residue Chemistry Branch
Hazard Evaluation Division (TS-769)

The petitioner, Dow Chemical USA, proposes to increase the
tolerances for combined residues of the pesticide chlorpyrifos,
0.0-diethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate and
and its metabolite 3,5,6-trichloro-2-pyridinol in or on food
commodities as follows:

<table>
<thead>
<tr>
<th>Food Crop</th>
<th>Tolerance Level</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>from</td>
</tr>
<tr>
<td>Sugar beet roots</td>
<td>0.2 ppm</td>
</tr>
<tr>
<td>Sugar beet tops</td>
<td>0.05</td>
</tr>
<tr>
<td>Dried sugar beet pulp</td>
<td>1.0</td>
</tr>
<tr>
<td>Sugar beet molasses for animal feed</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The petitioner also proposes in the amendment to revise
the 2 ppm tolerance for these pesticide residues in cattle
meat to express the tolerance in terms of the fat basis.
This attempt to make the U.S. tolerance coincide with the Codex Alimentarius Commission tolerance for cattle meat.

Tolerances are already established for residues in or on various raw agricultural commodities in 40 CFR 180.342. Tolerances range from 0.05 ppm to 15 ppm. The tolerance in milk fat is 0.5 ppm, in eggs is 0.1 ppm, in fat, meat and meat by-products of hogs, horses, goats and sheep is 1 ppm, in fat, meat, and meat by-products of cattle is 2 ppm, and in poultry fat, meat and meat by-products is 0.5 ppm.

Also, there are various food additive regulations for residues of chlorpyrifos and TCP in 21 CFR 193.85 and 561.98.

Conclusions

1. The nature of the residues of chlorpyrifos is adequately understood. The residues of concern are the parent compound and its metabolite 3,5,6-trichloro-2-pyridinol (TCP).

2. A satisfactory method is available in PAM II for enforcement purposes.

3a. Residues in roots and tops range up to 0.96 and 6.5 ppm, respectively. The proposed tolerances are adequate to cover these levels.

3b. The proposed food/feed additive tolerances are adequate to cover residues expected in these commodities from the proposed use.

3c. Data indicate that the tolerance expression for combined residues of the parent compound and its metabolite TCP in cattle should not be in terms of the fat basis. TCP, unlike chlorpyrifos, does not appear to concentrate in the fatty tissue. This is evidenced in both the current data submitted and data submitted in an earlier petition which supported establishment of the meat tolerances (PP#3F1306).

Also, it would be inappropriate to revise the tolerance expression for cattle and not revise that for other livestock since we expect similar metabolism of chlorpyrifos in these animals. An expression of the tolerance on the fat basis would not align the U.S. tolerances with Codex because the Codex tolerance is for chlorpyrifos alone instead of combined residues of chlorpyrifos and TCP.

While we are concerned to, wherever possible, make our U.S. tolerances compatible with Codex, we believe that any tolerance expression should include TCP. TCP is the major residue in non-fatty tissue. Liver, for example, could contain up to 2 ppm TCP from currently registered uses.
4. Tolerances already established for meat, milk, poultry and eggs are adequate to cover residues resulting from the proposed use.

Recommendations

We recommend against revising the current tolerance of 2 ppm in meat of cattle to be expressed in terms of fat basis (see conclusion 3c).

Toxicology and EFDB considerations permitting, we recommend for establishment of the tolerances of 1 ppm for sugar beet roots; 8 ppm for sugar beet tops; 5 ppm for sugar beet pulp; and 15 ppm for sugar beet molasses.

Detailed Considerations

Formulation

Lorsban® 4E (EPA Reg. No. 464-448) is proposed for use. The formulation contains 40.7% chlorpyrifos (4 lb ai/gal) and the inert ingredients and cleared in 40 CFR 180.1001.

Proposed Use

Chlorpyrifos is to be used for control of armyworms and cut worms in sugar beets. Both aerial and ground applications on foliage are employed at rates of 3/4 to 1 lb ai/Acre. There is to be a 30 day PHI for beet roots and tops and a maximum application of 8 pts (4 lbs ai) per season is allowed. There are also restrictions against grazing livestock in treated areas and harvesting treated tops for feed for meat or dairy animals within 30 days after last application.

In addition to the foliage-use, there is an at plant or early post emergence use on sugar beets reflecting application of the granular formulation (see PP#6F1786).

Nature of Residue

No data were submitted with this petition. Plant metabolism data are available on beans and corn and animal metabolism data are available on rats and chickens. These data were reviewed with PP#s, 3P1306 (see memo of 3/1/73, F. Gee) and 4P1445 (see memo 5/3/74, A. Smith).

The results of these studies show that chlorpyrifos and its metabolite 3,5,6-trichloropyridinol (TCP) are absorbed and translocated in plants. The significant product of chlorpyrifos metabolism is TCP which could be metabolized via dechlorination of the ring, formation of diols and triols and subsequently cleavage of the pyridine ring.
The nature of the residues of chlorpyrifos is adequately understood. The significant residues in both plants and animals are the parent compound and its metabolite, TCP.

Analytical Method

The analytical method used for determining residues of chlorpyrifos in sugar beet roots and tops is the same as the one used for determining these residues in lima and snapbean forage and beans. The method ACR 71.19R is listed in PAM II Method VII, as approved for determining chlorpyrifos residues.

The principle of the method is that all chlorpyrifos is hydrolyzed to 3,5,6-trichloro-2-pyridinol (TCP) so that the residues are determined as TCP and calculated back to chlorpyrifos equivalents. Since some TCP is likely to be present prior to the hydrolysis step, the conversion to chlorpyrifos would tend to give higher than actual residue results.

The sugar beet sample is heated and extracted with methanol in a basic medium. An aliquot is acidified and partitioned with benzene which is chromatographed on an acidic alumina column. The column is eluted with diethyl ether which is partitioned with sodium bicarbonate solution followed by acidification and partitioning with benzene. An aliquot of the benzene phase is treated with N,N-bis(trimethylsilyl) acetamide (BSA) to form the pyridinol trimethylsilyl derivative which is determined by gas chromatography using electron capture detection.

The average recovery was 90% in sugar beet roots at fortification levels from 0.025-5 ppm. The average recovery was 89% for sugar beet tops at fortification levels from 0.5-20 ppm.

Adequate methodology is available for enforcement purposes.

Residue Data

Two formulations containing chlorpyrifos were used in the residue studies in plots in California, Michigan, Nebraska and North Dakota. Lorsban® 15G, a granular formulation, was applied at the time of planting in 5,6 and 7 inch bands at a dosage of 9oz/1000 ft of row (1.5 lbs ai/A). This is followed by four foliar applications of Lorsan® 4E at the dosage of 1 lb ai/A. (A maximum of 4 lb ai/season is recommended for foliage application.)

Samples of sugar beet roots and tops were collected for residue analysis at 0, 15-16, 29-30 and 43-45 days following
last application (30 day PHI recommended). The sugar beet root samples were rinsed with cold water to remove soil particles. Both roots and tops were frozen soon after collection and shipped with dry ice to the laboratory for analysis. (Fortified samples of roots and tops stored at 18°C for 3.75 yrs. yielded average recoveries of 95 and 84% respectively.)

Residues, calculated as chlorpyrifos, for 29 and 30 day PHI's ranged from 0.04 to 0.96 for sugar beet roots and from 0.12 to 5.5 for tops. In two cases, for studies in California and Michigan, residues were higher in tops at a 45 day PHI than at a 30 day PHI. The highest residue was up to 6.5 ppm. The data indicate that the proposed tolerances for sugar beet roots and tops are adequate to cover residues that may result from this use.

Sugar Beet Pulp and Molasses

No data were submitted with this petition to show the concentration of residues in the processing of sugar beet roots. Reference is made to PP#6P1745 in which data indicate concentration factors of 3.7 for residues in sugar beet pulp and 13.8 for sugar beet molasses. Food additive tolerance levels for pulp and molasses were established at 5X and 15X concentrations respectively relative to the level established for beets.

The proposed tolerances in this petition for these same processed commodities are based on those same concentration factors. The proposed molasses and dried pulp tolerances are adequate.

Meat, Milk, Poultry and Eggs

Sugar beet products are considered as feed items for livestock and poultry. No feeding studies were submitted with this petition. Data are available, however, showing feeding studies with beef and dairy cattle, swine, and chickens. (PP#3P1306).

Cattle were fed 3, 10, 30, and 100 ppm chlorpyrifos in their daily diets for 30 days. Analyses of tissues showed that residues of chlorpyrifos were more highly concentrated in the fatty tissue and those of TCP were concentrated in muscle, liver and kidney. Residues ranged up to 4.70 ppm of chlorpyrifos in fat at 100 ppm. At 30 ppm feeding level the maximum residues found were 1.09 ppm chlorpyrifos in fat and 1.67 ppm TCP in liver.

A theoretical maximum residue from the established tolerances for chlorpyrifos (apple pomace at 12 ppm included
in this calculation) on various feed items comprising 100% of the cattle diet is ca. 14.4 ppm. The current established tolerance of 2 ppm for cattle tissue is adequate to cover this level. The dietary contribution for feed item products of sugar beets would be much less than this theoretical maximum. Thus, no additional feeding study for cattle is required.

The same result obtains for other livestock, milk, poultry, and eggs. We consider the tolerances already established for meat, milk, poultry and eggs adequate to cover any added contribution of sugar beet feed items to the diet.

Other Considerations

Cattle Meat

The petitioner proposes to revise the current tolerance of 2 ppm in cattle meat to express it as 2 ppm on fat basis. He contends that this proposal would make the tolerance consistent with the current CODEX tolerance. This is not the case. The CODEX tolerance is for the parent compound chlorpyrifos only. It does not include the metabolite TCP as does the U.S. tolerance.

The petitioner does not indicate that any changes should be made in the tolerance for cattle fat or cattle meat byproducts. Neither are any changes proposed for the meat tolerances of other livestock with established tolerances. Both the newly proposed cattle meat tolerances as well as the already established livestock tolerances are expressed in terms of chlorpyrifos and TCP.

The limited data submitted by the petitioner indicate that residues of chlorpyrifos are concentrated in the fat. However, TCP shows a propensity for concentration in the non fatty tissue. The average relative amounts of TCP compared to chlorpyrifos (where both compounds are found) are shown below:

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Chlorpyrifos</th>
<th>TCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscle</td>
<td>7X</td>
<td>2X</td>
</tr>
<tr>
<td>Fat</td>
<td></td>
<td>73X</td>
</tr>
<tr>
<td>Liver</td>
<td></td>
<td>60X</td>
</tr>
<tr>
<td>Kidney</td>
<td>2X</td>
<td></td>
</tr>
<tr>
<td>Milk</td>
<td></td>
<td>6X</td>
</tr>
</tbody>
</table>

The petitioner implies (letter of 7/9/82, R. B. Bischoff to Jay Ellenberger) that due to the lipophilic nature of chlorpyrifos and the approximate fat content of lean meat essentially all chlorpyrifos residues are in fat tissue. This does not follow for TCP as indicated in the above chart.
Thus, the data submitted does not support revising the tolerance to express it in cattle meat on the fat basis since it involves both the parent compound and TCP. Also, such expression does not coincide with the CODEX tolerance since the CODEX tolerance is for chlorpyrifos only.

We recommend that the expression for chlorpyrifos and TCP residues not be revised to "fat basis" for cattle meat.

Furthermore, we do not recommend deleting TCP from the meat tolerances. TCP is the major residue in some meat cuts as well as in some crops at certain intervals after treatment. For example, liver could be expected to contain 1.5-2.0 ppm of TCP from various registered uses of chlorpyrifos. Liver is recommended in the diet of the infant and is used as a pureed baby food. Consequently, we believe that TCP should continue to be included in the chlorpyrifos tolerance.

The Canadian tolerance for meat and meat by-products of cattle is expressed in terms of both chlorpyrifos and TCP. The tolerance level is 1 ppm as compared to 2 ppm U.S. tolerance.

The attached International Residue Limit Status sheet give additional information concerning related international tolerances.
INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Chlorpyrifos

CCPR NO. 17

Codex Status

No Codex Proposal
Step 6 or above

Residue (if Step 9): Chlorpyrifos only

<table>
<thead>
<tr>
<th>Crop(s)</th>
<th>Limit (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sugarbeets</td>
<td>0.051/</td>
</tr>
<tr>
<td>cattle,</td>
<td></td>
</tr>
<tr>
<td>carcass meat</td>
<td>- 2 (in the carcass fat)</td>
</tr>
<tr>
<td>sheep,</td>
<td></td>
</tr>
<tr>
<td>carcass meat</td>
<td>- 0.2 (in the carcass fat)</td>
</tr>
</tbody>
</table>

CANADIAN LIMIT

Residue: presumal

chlorpyrifos only except the animal products which include 3,5,6-trichloro-pyridinol

<table>
<thead>
<tr>
<th>Crop</th>
<th>Limit (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sugarbeets</td>
<td>0.12/</td>
</tr>
<tr>
<td>meat and</td>
<td></td>
</tr>
<tr>
<td>meat byproducts of cattle, except liver and kidney</td>
<td>1.0 (calc. on fat content)</td>
</tr>
<tr>
<td>liver and</td>
<td></td>
</tr>
<tr>
<td>kidney</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Notes: 1/ at or about limit of determination
2/ Negligible residue type tolerance.

PETITION NO. 2F2684

Reviewer: Jesse E. Mayes

Proposed U.S. Tolerances

Residue: Chlorpyrifos and 3,5,6-trichloro-2-pyridinol

<table>
<thead>
<tr>
<th>Crop(s)</th>
<th>Tol. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sugarbeet roots</td>
<td>1</td>
</tr>
<tr>
<td>sugarbeet tops</td>
<td>8</td>
</tr>
<tr>
<td>sugarbeet pulp</td>
<td>5</td>
</tr>
<tr>
<td>sugarbeet molasses</td>
<td>15</td>
</tr>
<tr>
<td>cattle meat</td>
<td>2 ppm in terms of fat basis</td>
</tr>
</tbody>
</table>

MEXICAN TOLERANCIA

Residue: 

<table>
<thead>
<tr>
<th>Crop(s)</th>
<th>Tolerance (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>(on sugar beets) or cattle</td>
</tr>
</tbody>
</table>

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