Evaluation of Pesticide Petition No. OP1003 for aldicarb (2-methyl-2-(methylthio)propionaldehyde o-(methylcarbamoyl) oxime) and/or its cholinesterase-inhibiting metabolites sulfoxide and sulfoxide

Submitted by Union Carbide Corporation
Filed July 27, 1970

INTRODUCTION

Other petitions 7F0573, 8F0637 and 9F0798.

The petitioner is proposing the following tolerances.

<table>
<thead>
<tr>
<th>Product</th>
<th>Tolerance (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar beet foliage</td>
<td>1.0</td>
</tr>
<tr>
<td>Sugar beet roots</td>
<td>0.05</td>
</tr>
<tr>
<td>Meat, fat, and meat products</td>
<td>0.01</td>
</tr>
<tr>
<td>Milk</td>
<td>0.002</td>
</tr>
</tbody>
</table>

The name of the product is: TEMIK 10G

DIRECTIONS FOR USE

Apply 15 to 30 lbs/A (1.5 to 3.0 lbs A/A) for insects and mites. Apply 40 to 50 lbs/A (4 to 5 lbs A/A) for nematodes. For insects: 3 applications /crop, one at planting and no more than two side-dress applications. No more than 6 lbs A/A/crop with a maximum dosage not to exceed 3 lbs A/A/application. For nematode: One application only, at planting time. No side-dress applications. PHI 90 days from harvest for beet roots. PHI 120 days from harvest for tops if fed to livestock.

ANALYTICAL METHOD

GLC, Colorimetric.

DISCUSSION OF DATA

Some of the data are listed below.

<table>
<thead>
<tr>
<th>Rate (lbs A/A)</th>
<th>Rate (lbs A/A)</th>
<th>PHI</th>
<th>Tops</th>
<th>Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 + 2 + 2</td>
<td>60</td>
<td>76</td>
<td>0.96</td>
<td>0.01</td>
</tr>
<tr>
<td>2 + 2 + 2</td>
<td>60</td>
<td>70</td>
<td>0.18</td>
<td>0.03</td>
</tr>
<tr>
<td>3 + 3 + 3</td>
<td>90</td>
<td>100</td>
<td>1.2</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>70</td>
<td>0.57</td>
<td>0.02</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>90</td>
<td>0.61</td>
<td>0.01</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>120</td>
<td>2.76</td>
<td>0.08</td>
</tr>
<tr>
<td>2 + 2 + 2 + 2 + 2</td>
<td>100</td>
<td>90</td>
<td></td>
<td>0.1</td>
</tr>
</tbody>
</table>
Total toxic residues in sugar beet tops treated with 10G Temik:

<table>
<thead>
<tr>
<th>Rate (Lbs A/A)</th>
<th>PHI</th>
<th>Aldicarb Sulfoxide Sulfone</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>120</td>
<td>0.02 0.07</td>
</tr>
<tr>
<td>4</td>
<td>140</td>
<td>0.03 0.14</td>
</tr>
<tr>
<td>5</td>
<td>114</td>
<td>0.17 0.73</td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>0.17 0.56</td>
</tr>
<tr>
<td>2 + 2 + 2</td>
<td>132</td>
<td>0.07 0.13</td>
</tr>
</tbody>
</table>

Analyses of fractions of sugar beet roots from sugar beets treated with 10G Temik:

| Rate (Lbs A/A) | PHI | Roots Diffusion Juice Thin Juice Thick Juice Dry Juice Wet Juice Pulp Sulfone |
|---------------|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1.6           | 139 | 0.005 0.005     | 0.001 0.005     | 0.001 0.005     | 0.001 0.005     | 0.001 0.005     | 0.001 0.005     | 0.001 0.005     |
| 8.0           | 156 | 0.011           | 0.011           |                 |                 |                 |                 |                 |
| 5.0           | 162 | 0.019 0.006     |                 |                 |                 |                 |                 |
| 2 + 2 + 2 + 2 + 2 | 139 | 0.006 0.006     |                 |                 |                 |                 |

Determination of Aldicarb and metabolites in sugar beets:

**Sugar Beet Foliage**

<table>
<thead>
<tr>
<th>PHI</th>
<th>Aldicarb</th>
<th>Aldicarb Sulfoxide</th>
<th>Aldicarb Sulfone</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.8</td>
<td>1.2</td>
<td>ND</td>
</tr>
<tr>
<td>14</td>
<td>0.7</td>
<td>0.98</td>
<td>ND</td>
</tr>
<tr>
<td>21</td>
<td>ND</td>
<td>1.13</td>
<td>ND</td>
</tr>
<tr>
<td>35</td>
<td>ND</td>
<td>0.62</td>
<td>ND</td>
</tr>
<tr>
<td>42</td>
<td>ND</td>
<td>0.32</td>
<td>ND</td>
</tr>
</tbody>
</table>

**Sugar Beet Root**

<table>
<thead>
<tr>
<th>PHI</th>
<th>Aldicarb</th>
<th>Aldicarb Sulfoxide</th>
<th>Aldicarb Sulfone</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>ND</td>
<td>0.03</td>
<td>ND</td>
</tr>
<tr>
<td>14</td>
<td>ND</td>
<td>0.05</td>
<td>ND</td>
</tr>
<tr>
<td>21</td>
<td>ND</td>
<td>0.05</td>
<td>ND</td>
</tr>
<tr>
<td>35</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>42</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

Metabolism of Temik Aldicarb in Sugar Beets:

Temik aldicarb was applied to sugar beets under green-house conditions at an exaggerated rate of 20 pounds A/A. Aldicarb sulfoxide, aldicarb sulfone and the non-toxic water soluble metabolites constituted the major portion of the resided C14 material. Most of the absorbed radioactivity was found in the foliage portion of the plant throughout the growing season. At (140 days after treatment) total C14 residues were 27.15 ppm in the foliage and 2.52 ppm in the roots. The corresponding values for total toxic residues (aldicarb sulfoxide and aldicarb sulfone) was 11.03 ppm in the foliage and 0.60 ppm in the roots.
After 28 days no aldicarb was detected in the plant. This is attributed to its high susceptibility to biological oxidation to form aldicarb sulfoxide.

<table>
<thead>
<tr>
<th>Days after Treatment</th>
<th>Aldicarb sulfoxide to Aldicarb sulfone ratio C-Mix soil, sandy loam</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>8.64</td>
</tr>
<tr>
<td>14</td>
<td>4.11</td>
</tr>
<tr>
<td>28</td>
<td>1.43</td>
</tr>
<tr>
<td>67</td>
<td>0.67</td>
</tr>
</tbody>
</table>

C-mix is a mixture of 1:1 of peat moss and read mortar sand.

The above table show the change with time in the ratio of aldicarb sulfoxide to aldicarb sulfone in sugar beet plants grown in 4 inch pots.

Water soluble metabolites were the most predominant single component in the plants at 90 and 140 days after treatment. The higher concentration of these materials in the roots than in the foliage suggests hydrolytic reactions and conjugation were more active in the subterranean portion of the plant.

Aldicarb sulfoxide to Aldicarb sulfone ratio. Sugar beet plants grown in 8 inch pots.

<table>
<thead>
<tr>
<th>Days</th>
<th>Foliage</th>
<th>Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.53</td>
<td>1.38</td>
</tr>
<tr>
<td>140</td>
<td>0.32</td>
<td>1.14</td>
</tr>
</tbody>
</table>

Aldicarb sulfoxide and aldicarb sulfone were the second highest components of the residues recovered from sugar beet plants. The total of the two metabolites consisted 39 percent and 23 percent of the terminal residues in the foliage and roots respectively. The ratio of aldicarb sulfoxide to aldicarb sulfone demonstrated a continuous conversion to the less toxic aldicarb sulfone.

Soil and Water

The chemical transformation of aldicarb and its movement in soil and water are reported in petition No. 9F0798. Aldicarb is biologically degraded by microorganisms in soil, reduced by uptake by growing vegetation, and chemically altered through the catalytic action of clays. The chemical changes that occur in soil are essentially the same as have been described for plants, animals and insects. Aldicarb is not readily moved downward through different soil types by leaching action and resultant contamination of ground water from Temik 10G treated fields is unlikely.
Cow Feed Study

A continuous feeding study using radiotracer techniques with lactating dairy cows is reported in petition no. 9F0798 and discussed in detail. The cows were fed 0.12, 0.6 and 1.7 ppm of a 1:1 molar ratio of 8-methyl Cl4 labeled aldicarb/aldicarb sulfone. The feeding was continued for 24 days, 10 days with non-radioactive pesticide followed by 14 days on radioactive material. There were no apparent harmful effects to the cows and no changes of blood cholinesterase levels, milk production, quantity of excretory products, or feed consumption.

About 90 percent of the administered dose was eliminated in the urine. After 14 days of feeding radioactive aldicarb at levels of 0.12 ppm, 0.6 ppm and 1.2 ppm residues were found in the milk at levels of 0.0014 ppm, 0.0057 ppm and 0.013 ppm respectively.

Total aldicarb residues in beef tissue:

<table>
<thead>
<tr>
<th>Tissue</th>
<th>Feeding Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.12</td>
</tr>
<tr>
<td>Liver</td>
<td>0.029</td>
</tr>
<tr>
<td>Kidney</td>
<td>-----</td>
</tr>
<tr>
<td>Heart</td>
<td>-----</td>
</tr>
<tr>
<td>Brain</td>
<td>-----</td>
</tr>
<tr>
<td>Neck muscle</td>
<td>-----</td>
</tr>
<tr>
<td>Front leg muscle</td>
<td>-----</td>
</tr>
<tr>
<td>Hind leg muscle</td>
<td>-----</td>
</tr>
<tr>
<td>Omental fat</td>
<td>-----</td>
</tr>
<tr>
<td>Subcutaneous fat</td>
<td>-----</td>
</tr>
</tbody>
</table>

The dash indicates that the levels were less than 0.004 ppm, the limit of sensitivity of the method.

CONCLUSION

We need to know what effect different moisture levels in soils would have on the residues found in sugar beet tops and roots?

Send the following with separate letter:

Clarification is needed on the soil data:

1. Are the half lives of aldicarb or aldicarb and its degradation products reported in all Temik petitions?

2. What is meant by percent recovered? Is this percent of applied labeled compound or percent total labeled found at a given time?

3. Some studies list water soluble residues and other unextractable residues are determined after a nitric acid digestion step. This indicate that aldicarb and its degradation product may be sorbed or bound in the soil. The non-extractable residues were not determined in the studies where
water soluble residues were found. We need to know if aldicarb is bound or sorbed in soil? We also note that the studies are done with different labeled molecules of aldicarb. The C¹⁴ (S-methyl) study indicated rapid lost in soil while S³⁵ did not. We can only conclude that the carbon in C¹⁴ (S-methyl) is lost and that the remainder of the molecule remains intact and persistent and/or sorbed in the soil. The soil studies do not show clearly what happens to aldicarb. We need to know the fate of aldicarb in soil. Perhaps aldicarb molecule labeled at C¹⁴ (S-methyl) and S³⁵ together or C¹⁴ tertiary work help determine its fate.

4. If aldicarb is water soluble we would like an explanation as to why there would be no runoff.

5. The analytical method for soil in Section D, Book II number 159 (UC 21149-111-soil) needs to be validated for recovery of weathered residues in soil.


RECOMMENDATION

No opinion is given. See conclusion.

Send PR Notice 70-15.
September 30, 1970

Subject: Pesticide Petition Number OP1008 requesting tolerances for Aldicarb (2-methyl-2-(methylthio) propionaldehyde O-(methylcarbamoyl) oxime and/or its cholinesterase inhibiting metabolites sulfone and sulfoxide, submitted by Union Carbide Corporation, and filed July 27, 1970

To: Charles L. Smith, Petition Control Office

We have examined the residue data, analytical methods, and other information in this petition for tolerances of 1.0 part per million (ppm) in or on sugar beet foliage, 0.05 ppm in or on sugar beet roots, 0.01 ppm in meat fat and meat by-products and 0.002 ppm in milk.

No opinion is given by this department for the following reasons:

1. We need to know what effect different moisture levels in soils would have on the residues found in sugar beet tops and roots.

2. Are half-lives reported in all Temik petitions as a half-life of aldicarb or aldicarb and its degradation products?

3. What is meant by percent recovered? Is this percent of applied labeled compound or percent of total found at a given time?

4. Some studies list water soluble residues and others unextractable residues. The unextractable residues are determined after a nitric acid digestion step indicating that aldicarb or its degradation products are sorbed or bound in soil. These residues were determined with S35 labeled aldicarb. The water soluble residues determined with Cl14 (S-methyl) aldicarb. The Cl14 study indicates that the methyl group or Cl14 is split off and that the rest of the molecule containing S35 may be present but not determined by Cl14 method. We need to know if aldicarb and its degradation products are bound or sorbed in soils? We need to know if moisture would release aldicarb or its degradation products from soil to be taken up by plants? The fate of aldicarb may best be determined by using a labeled molecule at both positions S35 and Cl14 (S-methyl) and/or Cl14 tertiary.

Literature has shown Temik formulation to be water soluble. We cannot understand why there would be no run off.

The analytical method for soil in Section D, Book II number 159 (UC 21149 - 111 - soil) needs to be validated for recovery of weathered residues in soil.

Mr. Smith send PR Notice 70-15.

Chemicals Evaluation Staff
ARS:PR:RENeY:FTSanders:mbS 9/30/70