POLYMER FORMULATIONS OF MOSQUITO LARVICIDES.

VIII. LABORATORY EVALUATIONS OF SELECTED POLYETHYLENE FORMULATIONS OF CHLORPYRIFOS

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ABSTRACT. Laboratory evaluations were conducted for 16 weeks to compare, under static conditions, residue levels maintained in water treated with three chlorinated polyethylene pellet formulations of chlorpyrifos [O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl) phosphorothioate]. All pellets were cylindrical in shape and had a specific gravity >1.0. Each formulation was evaluated at dosages of 0.25, 0.5, and 1.0 ppm. At equivalent dosages, there were no significant differences among average weekly residues maintained by the formulations, and for each formulation higher dosages produced significantly higher average weekly residues. Average weekly residues for all formulations and dosages peaked by week 8, decreased, and began to increase again by week 16. One of the three formulations was determined to be suitable for field testing due to its desirable toxicant to carrier ratio.

Studies reported by Nelson et al. (1970) showed that increases in percent composition of polyvinyl chloride (PVC) formulations of chlorpyrifos [O,O-diethyl-O(3,5,6-trichloro-2-pyridyl) phosphorothioate] caused an increase in release rate and residue levels maintained in water. Stockman et al. (1970) reported the theoretical effects of pellet size on the release rate of tributyltin oxide from rubber, and showed that the concentration released from formulations of different pellet size increased geometrically with decreasing pellet size (i.e., increasing surface to volume ratio). Stockman et al. (1970) also reported a linear relationship between percent composition of pesticide in a polymer and release rate. Studies conducted by Nelson et al. (1973) on eight chlorinated polyethylene (CPE) formulations of chlorpyrifos showed that significant increases in the average residues maintained in water occurred with increases in the surface to volume ratio of the pellets. Three CPE formulations of chlorpyrifos, differing from those tested by Nelson et al. (1973), were evaluated during the present study to determine residue levels maintained in water under static laboratory condition during a 16-week period.

MATERIALS AND METHODS

Formulations. The CPE pellet formulations evaluated in this study were provided by the Dow Chemical Company, Midland, Michigan, and were designated: M-3712, containing 5.6 percent chlorpyrifos and having a surface to volume ratio (s/v) of 4.82; M-3713 containing 5.6 percent chlorpyrifos and with s/v=4.40; and M-3714, containing 9.7 percent chlorpyrifos and with s/v=4.40. All pellets were cylindrical in shape and had a specific gravity >1.0. Additional physical characteristics of the formulations are given in Table 1.

Laboratory Tests. Each formulation was evaluated at dosages of 0.25, 0.50 and 1.0 ppm active ingredient, based on a theoretical total initial release. Treatments were replicated three times in individual 1-gallon glass jars containing 3 liters of
distilled water (pH 6.5) at room temperature. Three replicate jars containing only distilled water served as controls. Jars were sealed with aluminum foil liners and screw-cap lids to minimize loss of water by evaporation. Water samples (10 ml) were taken weekly from 1 through 16 weeks after treatment. The samples were extracted with hexane and analyzed by electron capture gas chromatography as described by Miller et al. (1973). The minimum detectable quantity measured in the water during the present study was 0.1 ppb chlorpyrifos.

Analysis of Data. Residue data were subjected to two way analysis of variance to determine the significance of differences due to the type of CPE formulation, dosage, and the interaction between the two. Differences among the means were determined by computation of the least significant difference at the 0.05 level of probability.

RESULTS AND DISCUSSION

Chlorpyrifos residues were maintained in all of the treated jars throughout the 16-week study. Specific average weekly residues maintained by each formulation at each dosage are shown in Figures 1, 2, and 3. Average residues for the three formulations over the 16-week test period did not differ significantly from each other (Table 2) probably due to insufficient differences in particle size and percent composition. However, the average residues did demonstrate the effects of particle size and percent composition. A comparison of M-3712 and M-3713, which were of the same percent composition but differing in particle size (Table 1), shows that M-3712, with the smaller particle size, maintained the higher average residue. This effect due to particle size was true for all dosages (Table 2). A comparison of M-3713 and M-3714, which were of the same particle size but differing in percent composition (Table 1), shows that M-3714, with the higher percentage, maintained the higher average residue. This effect due to percent composition was also true for all dosages (Table 2).

There was no significant interaction between formulation and dosage (Table 2), higher dosages resulting in significantly

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Percent chlorpyrifos</th>
<th>Diameter (mm)</th>
<th>Length (mm)</th>
<th>Volume (mm³)</th>
<th>Surface (mm²)</th>
<th>S/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-3712</td>
<td>5.6</td>
<td>1.0</td>
<td>2.5</td>
<td>1.96</td>
<td>9.45</td>
<td>4.90</td>
</tr>
<tr>
<td>M-3713</td>
<td>5.6</td>
<td>1.0</td>
<td>5.0</td>
<td>3.92</td>
<td>17.27</td>
<td>4.40</td>
</tr>
<tr>
<td>M-3714</td>
<td>9.7</td>
<td>1.0</td>
<td>5.0</td>
<td>3.92</td>
<td>17.27</td>
<td>4.40</td>
</tr>
</tbody>
</table>

* Coded designations provided by the Dow Chemical Company.

Table 2.—Average residue levels maintained in laboratory jars treated with three polymer formulations of chlorpyrifos at dosages of 0.25, 0.50, and 1.00 ppm.

<table>
<thead>
<tr>
<th>Formulation*</th>
<th>0.25 ppm dosage</th>
<th>0.50 ppm dosage</th>
<th>1.0 ppm dosage</th>
<th>All dosages</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-3712</td>
<td>20.0 a</td>
<td>40.1 b</td>
<td>63.0 c</td>
<td>41.0 b</td>
</tr>
<tr>
<td>M-3713</td>
<td>18.7 a</td>
<td>36.9 b</td>
<td>57.5 c</td>
<td>37.7 b</td>
</tr>
<tr>
<td>M-3714</td>
<td>19.2 a</td>
<td>42.1 b</td>
<td>57.7 c</td>
<td>39.6 b</td>
</tr>
<tr>
<td>All formulations</td>
<td>19.3 a</td>
<td>39.7 b</td>
<td>59.4 c</td>
<td></td>
</tr>
</tbody>
</table>

* Coded designations provided by the Dow Chemical Company.
** Averages followed by the same letter do not differ significantly at the 0.05 level of probability.
Fig. 1.—Average weekly residues observed in water dosed at 0.25, 0.5, and 1.0 ppm with CPE pellets containing 5.6 percent chlorpyrifos and having a surface to volume ratio of 4.90.
Fig. 2.—Average weekly residues observed in water dosed at 0.25, 0.5, and 1.0 ppm with CPE pellets containing 5.6 percent chlorpyrifos and having a surface to volume ratio of 4.40.
Fig. 3.-Average weekly residue observed in water dosed at 0.25, 0.5, and 1.0 ppm with CPE pellets containing 97 percent chlorpyrifos and having a surface to volume ratio of 4:40.
higher average residues, regardless of formulation. Since this was the case, the effects of dosage for the combined formulations were analyzed by polynomial regression tests to determine if a correlation existed between dosage and weeks after treatment. These polynomial regression tests showed that a highly significant (p < .01) correlation existed between average chlorpyrifos residues and weeks after treatment at each dosage level. The correlation curves for each dosage level were best described by third degree polynomial equations (Figure 4). The correlation coefficients for each dosage level were not significantly different (p > .01). Plotting the curves described by the third degree polynomial equations (Figure 4) showed a pattern where, at all dosages, residue levels peaked by week 8, decreased, and began to increase again by week 16.

CONCLUSIONS

Any of the three formulations evaluated during this study would be a suitable candidate for further evaluation against natural populations of mosquitoes under actual field conditions because there were no significant differences among residue levels maintained. However, in the field application of slow-release formulations the

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**Fig. 4.—** Relationship of average chlorpyrifos residues maintained in water by chlorpyrifos-CPE pellets to week after treatment when dosed at 0.25, 0.5, and 1.0 ppm.
relative amount of formulation which would be required (kg/hectare) to give comparable dosages as evaluated in the laboratory is of primary importance. For example: to dose an area at 1.0 ppm would require 54.9 kg/hectare\(^6\) for either M-3712 or M-3713 (5.6 percent AI) whereas, M-3714 (9.7 percent AI) would require only 31.1 kg/hectare. The other dosages would be similarly related. The favorable decrease in the amount of M-3712 required is a result of its higher toxicant to carrier ratio. Reduction of the total weight of formulation needed to treat any particular area would: (1) significantly decrease the cost of treatment, (2) decrease the amount of carrier residue which would remain after the formulation had lost its effectiveness and (3) increase the amount of area that can be treated at any one time, especially when dispersed by aerial application from light planes or helicopters. M-3714 is considered the most promising of the three formulations for field evaluation since it has the most favorable toxicant to carrier ratio.

References Cited


\(^{6}\) All references to dosage, whether stated as ppm or kg AI/hectare, are pounds AI/acre-foot equivalents.

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