# LABORATORY STUDY OF THE RELEASE OF SOME ORGANIC PHOSPHORUS INSECTICIDES INTO WATER FROM GRANULAR FORMULATIONS

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The effectiveness of granulated insecticides against mosquito and sand fly larvae, particularly when a heavy cover of vegetation must be penetrated, has been pointed out by Whitehead (1951), Keller *et al.* (1954a, b), and Labrecque and Goulding (1954). Labrecque *et al.* (1956) reported studies comparing size and composition of granular formulations for control of mosquito larvae by the use of bio-assay tests both in the laboratory and field. Collins (1955) has pointed out the need for more information on the physical characteristics of formulations for a better understanding of their use in insect control. Since there is very little information on the properties of granulated insecticides, chemical assays were conducted at the Orlando, Fla., laboratory to study the behavior and release of some organic phosphorus insecticides into water when applied as granular formulations.

MATERIALS AND GENERAL METHODS. Five types of granular carriers—attapulgite (Attaclay), montmorillonite (KWK Volclay, bentonite), vermiculite, diatomite (Celite), and pyrophyllite (Pyrax)—were used in the tests. Attapulgite, vermiculite, diatomite, and pyrophyllite were screened to 16/20 mesh and montmorillonite to 20/30 mesh. Most tests were run with parathion, but limited studies were conducted with Chlorthion and EPN. Granular formulations were prepared by saturating the carriers with acetone solutions of the insecticides and evaporating the acetone with an air stream. Since acetone swelled and dispersed montmorillonite granules, benzene was used in its place. In some tests kerosene or Velsicol AR–60 was used as a solvent and/or Triton X-100 as a wetting agent. The insecticides were extracted from water with benzene and analyzed by the method of Averell and Norris (1948).

Tests using 250 to 400 ml. of water were made in glass jars 3⅛ inches in inside diameter, and those using 1 liter of water were made in beakers 4 inches in diameter. Samples of water for testing were withdrawn by aspiration to minimize disturbance. The temperature ranged from 80° to 90° F. From 2 to 6 replicates of each test were made.

TESTS WITH PARATHION. The first experiment was conducted to determine whether the parathion released into water was distributed equally. Two grams of attapulgite containing 1 percent of parathion were added to 1 liter of distilled water to give 20 p.p.m., and allowed to stand 24 hours. Then 25-ml. volumes were sampled at different levels in the container. After the sampling all but the bottom ¼ inch of water was aspirated and discarded, the granules were filtered from the remaining water, and a 25-ml. sample of the filtrate was analyzed. No appreciable difference in the concentrations of parathion was found in the samples from the top, middle, and ¼ inch from the bottom, being respectively, 3.9, 4.1, and 3.6 p.p.m. The filtrate from around the granules gave a concentration of 8.3 p.p.m., approximately twice that in the three other locations.

The next experiment was to determine the quantity of parathion released into 250 ml. of distilled water by 1.0-, 0.5-, and 0.25-gram samples of attapulgite containing 1 percent of parthion. After standing 24 hours, water samples from the middle of the water column were analyzed. Then 240 ml. of the water were aspirated and discarded and a new 240-ml. volume added. After another 24 hours other

TABLE 1.—Release of parathion into distilled water from different amounts of 1 percent attapulgite granules

| Weight of Granules (grams) | First Volume of Water | | Second Volume of Water | | Total Percent |
|---|---|---|---|---|---|
| | p.p.m. | Percent | p.p.m. | Percent | |
| 1.00 | 10.2 | 25 | 8.6 | 21 | 46 |
| .50 | 6.9 | 35 | 6.4 | 30 | 65 |
| .25 | 5.8 | 58 | 2.5 | 23 | 81 |

samples were analyzed. The results given in Table 1 show that increasing the quantity of granules increased the concentration of toxicant present in the water but reduced the percentage of the total released.

The rates of release of parathion into distilled water from 1- and 10-percent granules on five carriers were compared. Either 500 mg. of 1-percent or 50 mg. of 10-percent granules were added to 250 ml. of distilled water in each of six glass jars, which were then covered with watch glasses. Each jar was allowed to stand for 1 to 9 days, and then 25 ml. from the middle of each water column were analyzed. From the jars that were tested on the fourth day 200 ml. of water were removed, a new 200 ml. was added, and the concentration of parathion was determined after 3 more days. Table 2 summarizes the results of these tests. The formulations with 1 percent of parathion on attapulgite, vermiculite, and diatomite showed a faster rate of release than those with 10 percent. With the passage of time differences between the two concentrations were reduced. Granules with 1 percent of parathion on vermiculite gave the highest initial release rate. There was very little difference between the two concentrations on montmorillonite, and they were lower than 1-percent formulations on attapulgite, vermiculite, and diatomite. The parathion already dispersed in the water had a tendency to reduce the release rate. When the water was changed after 4 days, the new water accepted more parathion over a 3-day period than that accepted between the fourth and seventh days when the water was not changed, but less than that accepted during the first 3 days, except with montmorillonite.

TABLE 2.—Release of parathion into distilled water from five granular carriers. Dosage, 20 p.p.m. of parathion

| Carrier | Percent of Parathion | In First Volume of Water (p.p.m.) | | | | | | In Second Volume of Water (p.p.m.) |
|---|---|---|---|---|---|---|---|---|
| | | 1 day | 2 days | 3 days | 4 days | 7 days | 9 days | 3 days |
| Attapulgite | 1 | 7.0 | 9.2 | 10.5 | 11.4 | 11.8 | 14.2 | 7.5 |
| | 10 | 3.4 | 5.8 | 7.7 | 7.8 | 10.2 | 11.8 | 6.7 |
| Montmorillonite | 1 | 5.0 | 6.7 | 6.2 | 6.8 | 7.9 | 9.0 | 7.0 |
| | 10 | 6.3 | 6.4 | 6.2 | 6.8 | 9.1 | 10.5 | 10.5 |
| Vermiculite | 1 | 9.2 | 9.5 | 11.8 | 12.0 | 13.0 | 13.1 | 7.7 |
| | 10 | 4.3 | 6.2 | 6.9 | 7.8 | 9.4 | 11.6 | 5.5 |
| Diatomite | 1 | 7.5 | 9.7 | 12.0 | 11.8 | 12.7 | 13.5 | 8.3 |
| | 10 | 3.9 | 5.4 | 6.7 | 8.0 | 9.2 | 10.7 | 5.1 |
| Pyrophyllite | 1 | 5.9 | 7.3 | 7.9 | 8.1 | 9.9 | 11.6 | 6.7 |

TABLE 3.—Adsorption of parathion after 24 hours on five granular carriers from water solutions containing 15.5 p.p.m.

| Carrier | Parathion Concentration after 24 hours (p.p.m.) | Percent Adsorbed |
|---|---|---|
| Attapulgite | 14.5 | 6 |
| Montmorillonite | 11.3 | 27 |
| Vermiculite | 14.4 | 7 |
| Diatomite | 13.9 | 10 |
| Pyrophyllite | 15.0 | 3 |

In the preceding tests, between 30 and 50 percent of the parathion was not released in 9 days. To determine whether adsorption was affecting the amount released, 1 gram of each of the granular carriers was added to 50 ml. of water containing parathion at 15.5 p.p.m. and shaken. Montmorillonite granules dispersed to form practically a colloidal suspension, so that it had to be centrifuged before sampling. Analyses of aliquots of the solution before and 24 hours after addition of granules showed that montmorillonite was the only material that gave a large amount of adsorption (Table 3).

TESTS WITH PARATHION, CHLORTHION, AND EPN AT 1 P.P.M. Tests indicate that the release rate is decreased as the water-saturation point is approached. The water solubility of parathion (20 p.p.m.) is approximately 2,000 to 20,000 times the concentration required for measurable toxicity response of mosquito larvae. At the concentrations used in tests against these larvae it is impossible to extract sufficient chemical for analysis. To obtain 50 micrograms from a 0.005-p.p.m. concentration would require extracting 10 liters of water. Consequently, the remaining tests were conducted at 1 p.p.m.

The amount of parathion released into distilled and marsh salt water from five granular carriers was determined. Either 100 mg. of 1 percent or 10 mg. of 10 percent granules were added to 1 liter of water in beakers, which were covered with watch glasses and allowed to stand 24 hours. Then 250 ml. from the middle of the water column were analyzed. Table 4 shows that, as in previous tests, 1 percent formulations on attapulgite, vermiculite, and diatomite released a greater amount than did 10 percent formulations. The two concentrations of parathion on montmorillonite released approximately the same amount into distilled water and gave the largest release. The amount released into marsh salt water was slightly less than that into distilled water except for the 10 percent montmorillonite granules, which showed a large decrease. The difference between the two concentrations is much greater in these tests than in those with parathion at 20 p.p.m. when attapulgite, vermiculite, and diatomite granules were used.

A series of tests were run to study the effect of including solvents and wetting agents in the formulation, or the presence of soil, on the amount of parathion released. Either 100 mg. of 1 percent or 10 mg. of 10 percent granules were added to 1 liter of distilled water, and 250 ml. of water sampled from the middle of the water column after 24 hours. The results, given in Table 5, show that the addition of 2 percent of kerosene or Triton X-100, or 1 percent of each, had no effect on the amount released in 24 hours from attapulgite, but the presence of Velsicol AR-60 or soil with diatomite granules reduced the quantity of parathion found in the

TABLE 4.—Parts per million of parathion released into distilled and marsh salt water in 24 hours from five granular carriers containing 1 and 10 per cent of the insecticide. Dosage, 1 p.p.m. of parathion

| | Distilled Water | | Marsh Salt Water | |
|---|---|---|---|---|
| Carrier | 1% | 10% | 1% | 10% |
| Attapulgite | .71 | .25 | .64 | .18 |
| Montmorillonite | .88 | .92 | .75 | .17 |
| Vermiculite | .85 | .30 | .63 | .12 |
| Diatomite | .81 | .21 | .71 | .18 |
| Pyrophyllite | .41 | * | .28 | * |

* Impossible to formulate 10 percent parathion on pyrophyllite granules.

TABLE 5.—Parts per million of parathion released in 24 hours from granules containing various solvents and wetting agents

| Carrier | Solvent or Wetting Agent | 1% Granules | 10% Granules |
|---|---|---|---|
| Attapulgite | None | .71 | .25 |
| | Kerosene 2% | .72 | .25 |
| | Triton X-100 2% | .70 | .25 |
| | Triton X-100 + kerosene, 1% each | .70 | .27 |
| Diatomite | None | .81 | ... |
| | Over 1 inch of soil | .56 | ... |
| | AR-60, 25% | .22 | ... |
| | AR-60, 25% over 1 inch of soil | .22 | ... |

water. A concentration of 0.81 p.p.m. was obtained from diatomite alone in 24 hours, whereas the concentrations obtained from diatomite plus 25 percent of Velsicol AR-60 were 0.37, 0.41, 0.56, and 0.49 p.p.m. after 2, 4, 7, and 8 days.

A series of tests were run to compare the amount of parathion, Chlorthion, and EPN released into water at 4, 8, 24, or 48 hours. Either 40 mg. of 1 percent or 4 mg. of 10 percent granules on five carriers were added to 400 ml. of distilled water and allowed to stand for 24 hours, and then a 250-ml. volume of water was aspirated for analytical determination. Table 6 shows that the 1 percent granules of both parathion and Chlorthion on attapulgite, vermiculite, and diatomite granules released toxicant more rapidly than 10 percent formulations. There was not a large difference in release of parathion or Chlorthion, but insufficient EPN was present for analysis, indicating a much lower release. Both formulations on montmorillonite released about the same amount of toxicant, which was about the same as or larger than on other carriers. Essentially total release of parathion was obtained in 48 hours from 1 percent attapulgite and 1 and 10 percent montmorillonite granules.

DISCUSSION. In these experiments granules containing 1 percent of parathion showed a faster rate of release than those containing 10 percent, at dosages of both 1 and 20 p.p.m., except when montmorillonite was used as the carrier. Since both 1 and 10 percent granules were applied at the same dosages of parathion, the greater surface exposed to water due to the larger quantity of carrier present was probably responsible. The montmorillonite granules used were a type of swelling bentonite, and this accounts for the high release of parathion from 10 percent granules at the lower dosage. Because the granules swell and disperse, they either present a larger surface area for release

TABLE 6.—Parts per million of parathion and Chlorthion released from five types of granular carriers containing 1 and 10 percent of the insecticides

| | 4 Hours | | 8 Hours | | | | 24 Hours | | | | 48 Hours | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Parathion | | Parathion | | Chlorthion | | Parathion | | Chlorthion | | Parathion | |
| Carrier | 1% | 10% | 1% | 10% | 1% | 10% | 1% | 10% | 1% | 10% | 1% | 10% |
| Attapulgite | ... | * | .40 | * | .38 | * | .62 | .11 | .53 | .28 | .97 | .47 |
| Montmorillonite | .42 | .14 | .57 | .59 | .51 | .65 | 1.15 | .76 | .58 | .54 | .97 | 1.01 |
| Vermiculite | .12 | * | .34 | * | .30 | * | .51 | .10 | .30 | .21 | .78 | .22 |
| Diatomite | .22 | * | .40 | * | .43 | * | .65 | .14 | .53 | .30 | .77 | .32 |
| Pyrophyllite | * | * | .35 | ... | .19 | ... | .41 | ... | .45 | ... | .52 | ... |

* Not enough chemical present in volume of water extracted for the limits of the analytical method.

or actually carry the parathion into the water when they disperse as colloidal particles. At the higher dosage 1 percent montmorillonite granules released less than did other 1 percent granules. Since it was shown that the release is decreased near the point of water saturation of parathion and since montmorillonite granules adsorbed this chemical from water solution in this range, the slower rate of release probably results from an adsorption mechanism. Montmorillonite granules did not swell and disperse in salt water as much as they did in distilled water. This accounts for the decrease in amount released from 10 percent montmorillonite granules into salt water. The release rate of parathion and Chlorthion was about the same, while that of EPN was much lower. Based on previous bioassay studies, parathion appeared about twice as soluble as Chlorthion, and more than 100 times as soluble as EPN; so water solubility is apparently a factor in release into water.

SUMMARY. In laboratory tests chemical analyses of water treated with granular formulations of parathion, Chlorthion, and EPN in five types of carriers were conducted to study the behavior and release of toxicants into water. Sampling different depths of water treated with attapulgite granules containing 1 percent of parathion showed a uniform distribution of the toxicant between the top and ¼ inch from the bottom after 24 hours. Increasing the quantity of granular formulation added to equal volumes of water increased the concentration of toxicant present, but decreased the percentage of the total released.

Granules containing 1 percent of parathion showed a faster rate of release than those containing 10 percent except when montmorillonite was used as the carrier. These differences were reduced with the passage of time. Both concentrations on montmorillonite released at approximately the same rate and were, for the most part, lower than other 1 percent formulations at a higher dosage (20 p.p.m.) and equal to or higher at a lower dosage (1 p.p.m.). Parathion was released slightly less rapidly into salt water than into distilled water from all formulations tested except the 10 percent concentration on montmorillonite, which showed a considerable decrease in the amount released in a given time. The addition of 2 percent of kerosene or Triton X-100 or 1 percent of each of these showed no effect on the amount released, but 25 percent of Velsicol AR-60 decreased the rate of release. The release rate of parathion and Chlorthion was about the same, while that of EPN was indicated to be much lower.

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