salis through mid-July. Mammalian burrows and rock fissures provided shelter for *C. tarsalis* and *A. freeborni* throughout the period of study. *C. tarsalis* preferred burrows in ground contact for resting, *A. freeborni* showed a preference for marmot burrows. While temperature and humidity within burrows to a depth of three feet varied little from the external environment during mid-afternoon, the maximum light intensity of good resting sites was less than ten foot candles during the same period.

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References Cited

Hubert, A. A., Rush, W. A., and Brennan, J. M. 1954. Simplified techniques for the continuous rearing of *Culex tarsalis* with additional notes and observations. Mosq. News 14:75–8.

Loomis, E. C. and Green, D. H. 1959. Ecological observations on *Culex tarsalis* Coquillett and other mosquitoes in the Delta region of the Central Valley of California, 1953–1956 (Diptera: Culicidae). Ann. Ent. Soc. Amer. 52:524–33.

Mortensen, E. W. 1953. Observations on the overwintering habits of *Culex tarsalis* Coquillett in nature. Proc. and Papers 21st Ann. Conf. Calif. Mosq. Control Assoc., pp. 59–60.

Ryckman, R. E. and Arakawa, K. Y. 1952. Additional collections of mosquitoes from wood rat's nests. Pan-Pac. Ent. 28:105–6.

Schmidt-Nielson, B. and Schmidt-Nielson, K. 1950. Evaporative water loss in desert rodents in their natural habitat. Ecology 31:75–85.

Stuntz, J. R. 1952. Observations of the distribution and overwintering behavior of adult *Culex tarsalis* and *C. stigmatosoma* during 1951. Report (unpublished) of Rice Field Mosq. Research Proj., Calif. Mosq. Control Assoc., pp. 1–17.

EFFECT OF TEMPERATURE ON RATE OF RELEASE OF TOXICANTS FROM GRANULES AND ON BREAKDOWN OF CERTAIN INSECTICIDES IN WATER[1]

MIR S. MULLA AND HAROLD AXELROD
University of California Citrus Experiment Station, Riverside

Introduction. The feasibility of using granular formulations of chlorinated hydrocarbon insecticides for the control of ricefield mosquitoes was investigated for the first time less than a decade ago (Whitehead 1951). It was suggested that aqueous sprays incompletely penetrated the plant canopy and that they resulted in erratic and sometimes poor control of *Psorophora* mosquitoes breeding in rice paddies. Granular insecticides were observed to penetrate the plant foliage and thus to reach the water below the plant canopy where the insects were breeding.

LaBrecque and Goulding (1954) obtained better and longer control of *Culicoides furens* (Poey) with granular BHC and dieldrin than with sprays, in a densely foliated salt marsh in Florida. Keller *et al.* (1954) attributed failure of sprays to control larvae of *Aedes taeniorhynchus* (Wied.) and of *A. sollicitans* (Wlkr.) in salt marshes to incomplete penetration of sprays through the dense foliage.

The efficiency of granular insecticides was demonstrated in the laboratory by obtaining good kill of *Anopheles quadri-*

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maculatus Say with granular insecticides (LaBrecque *et al.* 1956). The rate of release or the temperature at which the tests were performed was not made known in this work. The results are probably dependent on the extent of release of toxicants as well as on the toxicity and stability of various materials studied. Hilsenhoff (1959) investigated the efficiency of granular insecticides against *Tendipes plumosus* (Linnaeus) with the water temperature maintained at 20° C. during the testing period.

Weidhaas (1957) initiated studies on the rate of release of parathion, EPN, and chlorothion into water. These studies were conducted at temperatures of 80° to 90° F. Good release was generally obtained for parathion and chlorothion, but release for EPN was poor.

In preliminary studies on the efficiency and performance of granular formulations, Mulla and Axelrod (1959) demonstrated the rate of release of organophosphate insecticides to be markedly influenced by the temperature of the water to which the granules were added. The studies reported herein concern the relation of temperature to the rate of release of toxicants from granular materials into water. To study this relationship more thoroughly, the rate of breakdown of some insecticides at various temperatures in water was also investigated.

MATERIALS AND METHODS. Samples of granular materials were prepared in the laboratory in a small rotary unit. The details of the formulating procedure of granules are presented elsewhere (Mulla and Axelrod 1960). Batches of 20–40 grams of the formulated materials were prepared for each test. The finished granular product was dust-free and was tested for rate of release 1 to 3 days after formulating.

Two percent granular parathion, Bayer 29493 (*O,O*-dimethyl *O*-3-methyl-4-methyl-4-methylthiophenyl phosphorothioate) and AC 5727 (*m*-isopropylphenyl N-methylcarbamate) and 5 percent granular malathion were made by preparing solutions from the technical materials, using isopropanol and Espesol 5 as solvents and impregnating the solution onto the granules. The solvents were used at 10 percent concentration of the finished product. The carriers used in all the experiments were attapulgite clay granules 30/60 mesh of the AA-LVM and AA-RVM type (Floridin Company, Tallahassee, Florida).

To determine the rate of release of the toxicants from the granules, various amounts of the 2 percent and 5 percent products were placed in a 1-gallon mayonnaise jar containing 3500 ml. of tap water having a pH of 8–8.5 and a height of 8.25 inches. This amounted to a 5 ppm concentration of the active ingredients of parathion, Bayer 29493, and AC 5727 in the water, provided the total quantities of the toxicants present were released. An amount of the 5 percent malathion formulation was added to the jar to yield a theoretical 20-ppm concentration of malathion in the water. Disturbance or stirring of the water was avoided after addition of the granules.

In the malathion and parathion tests, 25 ml. of water were aspirated from the top and bottom portions (1 inch above the granules) of the water column and composited for further dilution. To make the final dilutions, aliquots of the composite sample were added to each of three pint cups containing 100 ml. of tap water and 25 fourth instar larvae of *Culex quinquefasciatus* Say. This resulted in obtaining a final theoretical concentration of 0.02 ppm for parathion, 0.3 ppm for malathion granules and 0.15 ppm for malathion emulsion. Bayer 29493 and AC 5727 granules were tested at 0.05 ppm and 0.1 ppm of final theoretical concentration. The emulsifiable concentrate formulations of these materials were tested at 0.01 ppm and 0.07 ppm final concentrations, respectively.

The mosquito larvae were exposed to the toxicants at a temperature of 75°–78° F., and the mortality was recorded 24 hours later. The magnitude of release at each interval and each temperature was calculated from the observed mortality of larvae by reference to dosage mortality lines established for each of the toxicants and the total amount of each added to the jar. The maximum release for the parathion, malathion, and AC 5727 formulations was 60+ percent. The designation in the figures below is presented as such, indicating the release to be higher than 60 percent. The maximum release obtained for Bayer 29493 was more than 30 percent.

For determining the rate of breakdown of the four toxicants employed in our tests, the same concentration of each material as for granules was obtained by adding small volumes of the emulsifiable concentrates to the water in the 1-gallon jar and stirring thoroughly. Prior to taking aliquots from the bottom and top portions, the water was completely agitated with a stirring rod. The following procedure was the same as that employed in the evaluation of granular materials. The contents of the toxicants in water were calculated by utilizing dosage mortality lines established for these materials against mosquito larvae used as bioassay test insects.

Tests on the solubility of each material in water were also conducted. Acetone solutions of the toxicants were added to water at the lowest tempertaure under which the materials were tested either as granules or emulsions. Parathion and Bayer 29493 were made at a concentration of 5 ppm; and malathion was made at a concentration of 20 ppm. Mosquito larvae bioassay tests indicated the full amount of the toxicants to be present after 2–3 hours. These tests showed that the solubility of these materials at the lowest temperature was higher than the concentrations used in the tests here. AC 5727 was added at 5 ppm and it was determined to be soluble in water at a concentration of 3.5 ppm, at 70° F. A release of 60–70 percent of this material from its granules

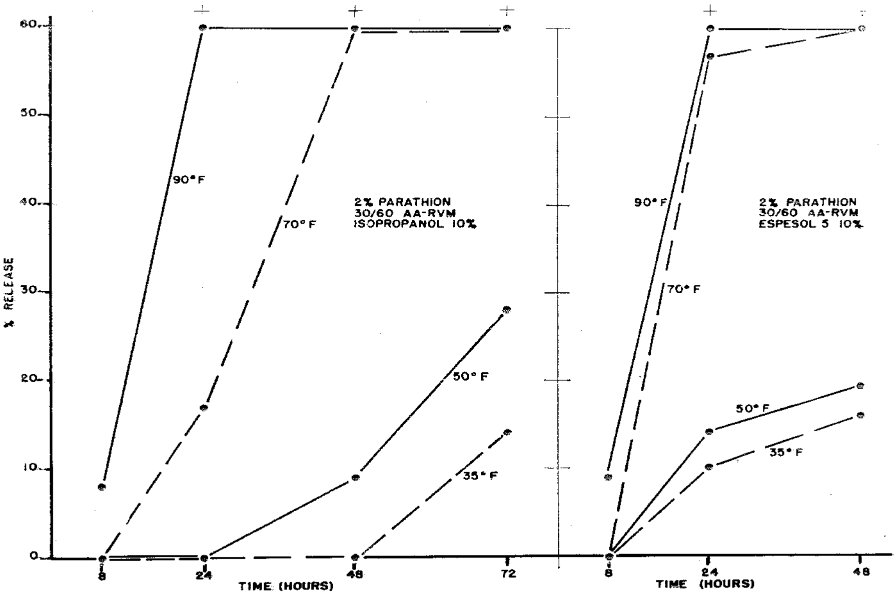

FIG. 1.—Pattern of release of parathion from granular formulations in water at various temperatures. The plus sign (+) indicates a release of > 60 percent.

as regulated by its solubility would represent 100 percent release of this toxicant.

RESULTS AND DISCUSSION. EFFECT OF TEMPERATURE ON RELEASE OF TOXICANTS. Parathion when impregnated on 30/60 AA-RVM attapulgite granules, using isopropanol and Espesol 5 as solvents for impregnation, yielded higher release at the higher temperatures (Fig. 1). The trend of release at the various temperatures was similar with both solvents, except that the release of the formulation using isopropanol as solvent at a temperature of 70° F. at the 24-hour interval was considerably lower than the release from the Espesol 5 formulation tested at the same temperature and the same period of exposure. The overall speed of release of parathion at 35°, 50° and 70° F. is greater for each sampling interval for the Espesol 5 formulation than for the isopropanol formulation. The differences, though small, are consistent over the entire range of the experimental temperatures.

The trend of the release of malathion for the three types of formulations used in the experiments was different from that of parathion. Here the release of malathion reached a maximum at the 8- or 24-hour period for temperatures of 80°, 90° and 100° F. and then started to decline rapidly (Fig. 2). At temperatures of 90° and 100° F., malathion hydrolyzed so rapidly that no appreciable quantities of malathion were detected after three days at a level of testing where 60 percent or more release was obtained initially. The overall release of the isopropanol formulation at 70° and 90° F. was lower than that of the Espesol 5 formulation.

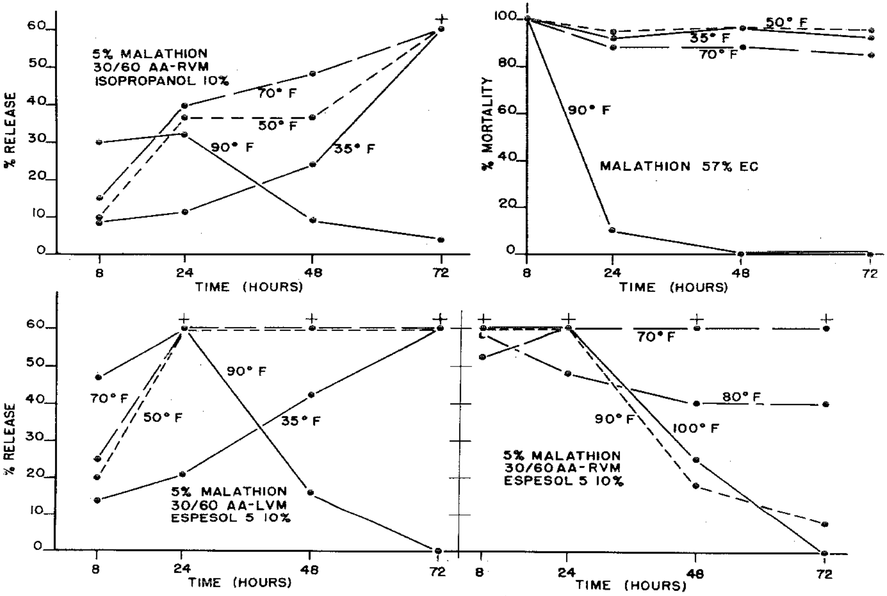

FIG. 2.—Rate of apparent release of malathion from its granular formulations, and the degree of breakdown in the emulsifiable concentrate form at various temperatures. The plus sign (+) indicates a release of > 60 percent.

The rapid decrease in the amount of malathion in water was at first thought to be induced by the type of granular formulation. However, further studies on the behavior of emulsifiable concentrate formulation of malathion revealed a similar rapid breakdown of malathion in the water at higher temperatures (see below).

The behavior of granular Bayer 29493 was found to be patterned after that of parathion, except that the magnitude of release of the former was much lower than that of the latter. The extent of release of Bayer 29493 from granules was also found to be a function of the temperature. The magnitude of release at all sampling periods was higher at higher temperatures (Fig. 3).

The release of AC 5727 from its granular formulation was completed at 8 hours' exposure for all temperatures (see Fig. 3). The level of AC 5727 in the water decreased after 8 hours and dropped rapidly at temperatures of 90° and 100° F. This rapid disappearance of AC 5727 was also determined for the emulsifiable concentrate formulation of this material at 100° F.

BREAKDOWN AT HIGH TEMPERATURES. Studies on the release of malathion from granular formulations established the fact that the malathion release from these formulations decreased in time within the temperature range of 70° to 100° F. This phenomenon was thought at first to be due to the readsorption characteristic of certain granular carriers as reported by Weidhaas (1957). However, studies on the quantity of malathion using emulsifiable concentrate formulations demonstrated a rapid decrease in the quantity of malathion in water between the time interval of 8 and 24 hours at 90° F. (see Fig. 2). There was

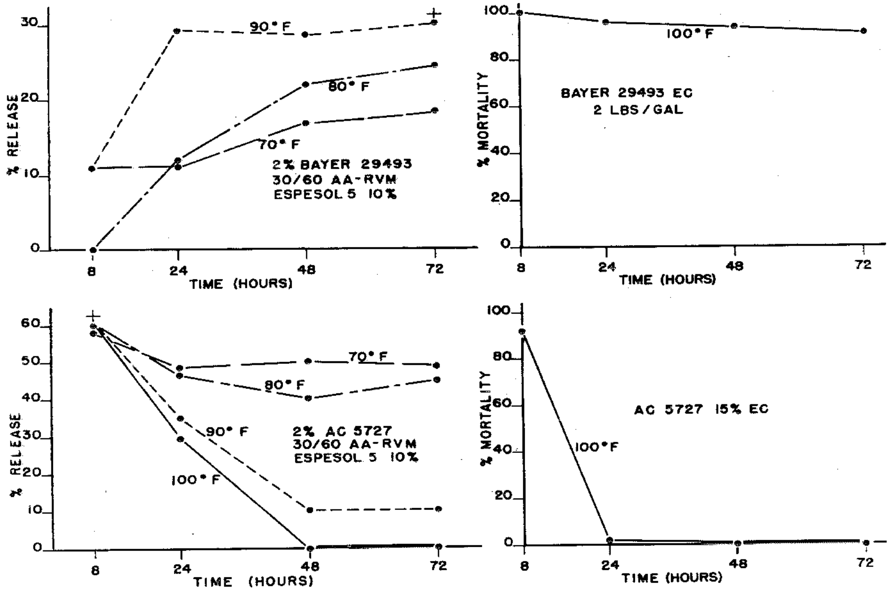

Fig. 3.—Behavior of granular and emulsifiable concentrates of Bayer 29493 and AC 5727 in water at various temperatures. The plus sign (+) indicates that the release was $>$ 30 percent and $<$ 60 percent for Bayer 29439 and $>$ 60 percent for AC 5727.

also a slight breakdown of malathion at a temperature of 70° F., but appreciable breakdown seems to result at higher temperatures.

Similar rapid decrease in the amount of AC 5727 was observed when the granular formulation of this material was tested for its release pattern at higher temperatures. The breakdown of this material was rather slight at 70° F. and 80° F., in comparison with that of malathion. At 90° and 100° F. there was a rapid breakdown of AC 5727 comparable to that of malathion. It should be pointed out that the rate of breakdown of the emulsifiable concentrate formulation of AC 5727 at 100° F. is greater at the beginning than that of its granular formulation. The granular formulation thus seems to increase the longevity of unstable materials somewhat over that of its emulsifiable concentrate formulation by not releasing the total amount of the toxicant into the water at once (see Fig. 3). Similar trends have also been observed for the two kinds of malathion formulations. A regulated release of unstable materials into water can be obtained by selecting the proper kind of solvent (Mulla and Axelrod 1960), thus lengthening the life of such materials in water over that of their emulsifiable concentrate formulations.

The breakdown of Bayer 29493 in the form of emulsifiable concentrate is relatively slight at 100° F. The release of this material from its granular formulation was observed to increase steadily with respect to time at all temperatures of the test (see Fig. 3). Because of the slight breakdown of this material at the elevated temperature (100° F.) it is considered to be stable. The stability of parathion under the test conditions at 100° F. was studied, but the magnitude of the breakdown of this material in water was negligible up to a period of 72 hours duration.

For mosquito larviciding programs under field conditions, stable materials as either granular or emulsifiable concentrate formulations are desirable. Stable materials not only maintain relatively constant concentration in infested waters but also take care of reinfestation for a longer period following treatments, as compared to relatively unstable toxicants. The longevity of many mosquito larvicides in the field has not been adequately studied. Studies in this direction should lead to the selection of more efficient materials and formulations as mosquito larvicides.

References

CHAPMAN, H. C. 1955. Tests with granulated and systemic insecticides against *Mansonia* larvae. Mosq. News 15(4):204–6.

HILSENHOFF, WILLIAM L. 1959. The evaluation of insecticides for the control of *Tendipes plumosus* (Linnaeus). J. Econ. Ent. 52(2):331–2.

KELLER, J. C., CHAPMAN, H. C., and LABRECQUE, G. C. 1954. Tests with granulated insecticides for the control of salt marsh mosquito larvae. Mosq. News 14(1):5–9.

LABRECQUE, G. C., and GOULDING, R. L. 1954. Tests with granulated BHC and dieldrin for controlling sand fly larvae. Mosq. News 14(1):20–2.

LABRECQUE, G. C., NOE, J. R., and GAHAN, J. B. 1956. Effectiveness of insecticides on granular clay carriers against mosquito larvae. Mosq. News 16(1):1–3.

MULLA, MIR S., and AXELROD, HAROLD. 1959. Granular formulations of insecticides and factors influencing their efficiency in mosquito control. Calif. Mosquito Control Assoc. Proc. 1959:79–82.

MULLA,, MIR S., and AXELROD, HAROLD. 1960. Efficiency of granulated insecticides influenced by solvents used for impregnation. J. Econ. Ent. (In press.)

WEIDHAAS, D. E. 1957. Laboratory study of the release of some organic phosphorus insecticides into water from granular formulations. Mosq. News 17(3):168–72.

WHITEHEAD, F. E. 1951. Rice field mosquito control by pellet-borne insecticides. Arkansas Agr. Expt. Sta. Bull. 511. 30 pp.