MOSQUITO CONTROL WITH MONOMOLECULAR ORGANIC SURFACE FILMS: I-SELECTION OF OPTIMUM FILM-FORMING AGENTS

WILLIAM D. GARRETT

Ocean Sciences Division, Naval Research Laboratory, Washington, D. C. 20375

AND

SHELDON A. WHITE

Navy Disease Vector Ecology, and Control Center, Naval Air Station, Jacksonville, FL 32212

ABSTRACT. Mosquito survival in the aquatic environment is highly dependent upon the nature of the air-water interface. Nonionic monomolecular organic films reduce surface tension and increase the wettability of larval and pupal breathing structures, thereby causing high mortality. Eclosing adults and those alighting on a film-covered surface are readily wetted and drowned.

The most effective and persistent agents are spontaneously spreading, surface-active liquids which reduce the aqueous surface tension to below 29 dynes/cm. In addition, the films displace natural scums and are self-healing after being disturbed by wind and waves. The films are effective in a natural paludal environment at a surface concentration of 0.04 milliliters per square meter (0.043 gallons/acre). Optimum properties of film-forming materials for the practical control of mosquitoes are itemized and related to chemical structural considerations.

INTRODUCTION. One long-used approach to mosquito control has been to prevent the emergence of the adult from its aquatic breeding sites through the use of petroleum-based oils. These antilarval oils may suffocate the larvae or kill them by specific toxicity. Nonvolatile hydrocarbon films containing only alkanes and cycloalkanes are slow in their physical impact on larvae. More rapid toxic effects appear to derive mainly from volatile aromatics and other toxic compounds drawn into the larval breathing tubes during respiration (Hagstrum and Mulla 1968). More recently, Berlin and Micks (1973) suggested that petroleum-based oils initiate larvicidal action by producing an irreversible hypoxia. Oil-soluble, surface-active agents are often added to petroleum oils to promote uniform spreading over the water surface against natural organic films and to enhance respreading after disruption by wind.

Another organic film approach to the control of the mosquito in water may be through the physicochemical modification of the aquatic surface with absorbed monomolecular films. The impact of reduced surface tension on the lifestyle of the mosquito in water caused by various concentrations of water-soluble, surface-active chemicals has been the subject of several entomological studies (Manzelli 1941, Russell and Rao 1941, Senior-White 1943, Fair et al. 1951, Singh and Micks 1957, Mulla and Chadhury 1968). The wetting and sinking of eggs laid at the surface was demonstrated, as well as the inability of pupae to maintain a proper breathing orientation at the water surface. Larvae had difficulty remaining at the surface when the surface tension had been reduced to a critical value, which varied between 27 and 36 dynes/cm and was species dependent. In general, lower surface tensions produced greater mortality rates. Pupal mortalities occurred at slightly higher surface tension values of from 36 to 41 dynes/cm.

The surface effects literature through 1967 was reviewed in detail by Wiltzius (1967) in a report concerned with the ecological effects of monomolecular films of commercial mixtures of n-alkanols used for the reduction of evaporation from reservoirs. Mosquito mortalities induced by the fatty alcohol monolayers in laboratory studies of *Aedes* were due primarily to effects on the pupae. A similar conclusion was reported by McMullen and Hill (1971), who reported a 100% rate of mortality to pupae of *Ae. aegypti* in laboratory studies with insoluble monolayers of various natural lipids. These lipid films produced little effect on the larvae of this species. Lauryl alcohol (1-dodecanol) monolayers were found to be variably effective against larvae and pupae of *Culex quinquefasciatus* (Lorenzen and Meinke 1968). Cumulative mortalities of 100% were realized after 72 hr, since adults were not able to emerge successfully from pupae at the water surface covered with the film of lauryl alcohol. In addition, it was determined that n-octanol did not produce a stable film, and that n-hexadecanol was ineffective. Msangi (1956) also concluded that n-hexadecanol (cetyl alcohol) had no appreciable influence on any of the aquatic forms of *Anopheles gambiae*. Many of these investigators have attributed the mortalities to physical effects of the surface-active chemical rather than to toxic influences.

SELECTION OF MOSQUITO-CONTROL FILM. Previous research has been performed primarily in the laboratory where the maintenance of a one-molecule-thick film in a small tray presents no problem. In the real environment monomolecular films would be subjected to a number of dispersive forces which act continuously to degrade an additive film. Air flow and surface currents are two very important factors, which also displace petroleum-based larvicidal oils. However, since mosquito-control films will be utilized primarily in relatively small, stagnant water bodies, the rate of film loss will be low for nonvolatile, water-insoluble compounds in the absence of strong winds.

It is necessary for film-forming chemicals and the surface films which they form to have certain physicochemical properties to assure not only effectiveness against aquatic forms of the mosquito, but also persistence and ease of application. These properties, listed below, are essential for optimum performance:

Highly surface active-reduction of water surface tension-displacement of natural films and scum-wetting of hydrophobic surfaces.
Liquid—easily and rapidly spread onto water surface.
Nonvolatile—relatively high molecular weight.
Low water solubility—large hydrophobic group in molecule—nonionic.
Fluid monomolecular film—rapid, spontaneous spreading
—high respreading potential.
Low freezing point.
Commercially available at reasonable cost.
Nontoxic, noncorrosive.

A relatively high molecular weight is required to ensure surface-film durability by providing low volatility and a low rate of dissolution into water. A nonionic structure is essential to prevent solubility losses into saline water due to the formation of soluble organic salts. Fluidity is desirable in the bulk material for ease of spraying and in the surface film for enhancing its rate of spread. Fluid films maintain a more uniformly reduced surface tension than rigid monolayers and respread readily after disruption by wind and waves when these stresses are relaxed. Highly branched hydrocarbon chains or chains which are permanently bent due to chemical unsaturation (cis isomers) increase fluidity in both the liquid and its surface film. Autophobicity is another important property of many of the liquid, water-insoluble, surface-active compounds; that is, they do not spread over their own monomolecular films. The excess liquid remains as a thick, oil-like lens in equilibrium with the spread film. When portions of the film have been degraded or displaced by natural forces, the excess material in the lens ("reservoir") immediately and spontaneously spreads to restore the equilibrium between the film and the excess bulk liquid, thereby maintaining uniform coverage and film pressure. Maintenance of fluidity at low temperatures is important because the surface spreading of liquids is orders of magnitude faster than that of solids.

As previously discussed, lowered surface tension may prevent the hanging of larvae, disrupt the upright orientation of pupae, sink floating eggs of certain species, and interfere with adult emergence. The reduction of the surface tension of water by a monomolecular film is a function of the balance between the hydrophobic and hydrophilic groups in the molecule as well as the chemical constitution of the outermost groups (toward the air) of the hydrophobic segment when the film is at its equilibrium spread condition. The water surface tension may be reduced to as low as 15 dynes/cm by perfluorooctanoic acid, and surface tensions almost as low are obtained with other highly fluorinated compounds (Jarvis and Zisman 1966). However, toxicity and cost considerations preclude the use of such materials in the aquatic environment.

Greatly lowered surface tension may be essential to produce larvicidal and pupicidal effects for another reason. Wetting of the internal hydrophobic structure of pupal and larval tracheae can lead to liquid blockage and interference with respiration. This will occur if the liquid surface tension is equal to or less than the critical surface tension of the solid (tracheal wall) in question. For example, Watson (1941) reported that the lining of the tracheae of anophoeline larvae appears to be a waxy substance. According to Zisman (1964), the critical surface tension of polyethylene ($-CH_2-$ surface structure) is 31 dynes/cm at 25°C. Since the internal tracheal wall will not be more hydrophobic than polyethylene, and since the chemicals used in this study reduced surface tensions below 29 dynes/cm, water blockage effects and wettability of waxy surfaces of larval and pupal tracheae are possible.

In consideration of the requirements just discussed, and of previously reported properties of a number of surface-active liquids (Garrett and Barger 1972, Barger and Garrett 1974), several nonionic organic liquids were selected as likely candidates for these mosquito-control studies. Distilled water was covered with a film of the liquid in equilibrium with a small excess lens. Surface tensions were measured at 25°C by the ring method using a Kruss du Nouy tensiometer. Surface tension of the film-covered water remained essentially constant over a period of 24 hours for the following liquid compounds and formulations used in this research.

In both laboratory and field experiments the films were applied at a surface concentration of 40 microliters per square meter. This value is about 20 times that required for a single monomolecular layer, and was used to provide an excess of chemical to resupply losses from the film. As mentioned previously, the excess mate-

Liquid	Composition	Surface tension
A	Diethylene glycol monolaurate	27.6 dynes/cm
B	Sorbitan monooleate, 75% 2-ethyl butanol, 25%	28.9 dynes/cm
C	Sorbitan monooleate, 37.5% lauryl ether containing 2 oxyethylene groups, 50% 2-ethyl butanol, 12.5%	28.3 dynes/cm
D	Isostearyl alcohol containing 2 oxeythylene groups	28.2 dynes/cm
E	Lauryl ether containing 4 oxyethylene groups	27.1 dynes/cm
F	Oleyl ether containing 2 oxyethylene groups	29.9 dynes/cm

rial did not spread over its own film, but remained as an unspread patch or liquid lens which acted as a reservoir to maintain complete coverage of the water surface. At this surface concentration it was possible to maintain an effective film under the conditions of these experiments for at least 24 hr.

POTENTIALITIES AND LIMITATIONS. Surface-active agents have been added to petroleum-based antilarval oils in recent years to enhance uniform spreading, displace natural films and scums on treated water bodies, and to reduce the quantity of petroleum required to treat a given area. The monomolecular organic surface films described in this research were developed as an alternative to petroleum films for mosquito control in the aquatic environment. If the purely surface-active, film-forming compounds prove to be successful against aquatic forms of the mosquito, the use of petroleum hydrocarbons on bodies of water can be reduced. Thus, curiously enough, the antilarval oils may be replaced by organic film-forming agents which are chemical relatives of the spreading agent presently incorporated into the petroleum based formulations.

In theory, a monomolecular layer of an organic substance or water represents an extremely small surface concentration. For example, each molecule of isostearyl alcohol containing 2 oxyethylene groups occupies a surface area of 30 square Angstroms at its collapse surface pressure. The theoretical minimum effective surface concentration would be 2.09 mg/m^2 or about 8.4 ml/acre. However, because of many natural dispersive factors which operate to degrade an additive organic film, an excess must be used in a realistic application of this method. In studies using the film-forming liquids the control agents were applied at a surface concentration of 0.04 ml/m^2, about 20 times that required for a monomolecular layer. This is a very small surface concentration when compared to the commonly used dosages of petroleum oils. Early techniques using petroleum as larvicidal oils required 45 ml/m^2 or more of material. By 1965 improvements in larvicidal petroleum oils reduced the required effective dosages to between 4.5 and 18 ml/m^2 (WHO, 1973). Recent advances through the incorporation of surface-active spreading agents into special petroleum fractions have reduced dose rates to about 2.8 ml/m^2 (3 gal./acre). Thus, there is a material advantage of at least 70 fold in using nonpetroleum surface films. This material advantage can be translated into reduced transportation and application costs. In addition, there will be a corresponding reduction in environmental stress on the treated water body due to (1) a lower oxygen demand because of less additive material and (2) less interference with gas exchange because of a thinner mosquito-control film.

One of the limitations of this method is the maintenance of complete coverage of a large body of water. Experience gained during the development of such water-insoluble surface films as oil-control agents and seamarkers (Barger and Garrett 1974) can be applied to this mosquito-control method. Because of the film-dispersive influences of wind and waves, total coverage of a large exposed water surface is difficult, especially when there is a long and constant wind fetch. Surface films are driven down wind, and unless film-forming material is continuously applied at the upwind end, the film is removed from large areas of the water surface. On the other hand, many mosquito larvae develop in small stagnant bodies of water. These include potholes, drainage ditches, discarded containers and tires, and small areas which are filled by rain or high tides. In swamps and marshes vegetation would protect the additive surface film against dispersal by wind. Thus, there are numerous possibilities for the use of mosquito-control surface films. Considerable additional experience is required under carefully monitored conditions to delineate the potentialities and limitations of this approach.

Literature Cited

Barger, W. R. and W. D. Garrett. 1974. Artificial sea slicks: their practical applications and role in fundamental research. Naval Research Laboratory Report 7751, 13 pp. (Washington, D.C.)

Berlin, J. A. and D. W. Micks. 1973. Cellular and subcellular effects of petroleum hydrocarbons on mosquito larvae. Ann. Entomol. Soc. 66:775–780.

Fair, G. M., S. L. Chang and F. E. Richart. 1951. Studies on anopheline larvae. II. The mechanisms involved in the flotation of larvae of *A. quadrimaculatus* on a water surface. J. Nat. Malaria Soc. 10:293–305.

Garrett, W. D. and W. R. Barger. 1972. Control and confinement of oil pollution on water with monomolecular surface films. Naval Research Laboratory Memorandum Report 2451, 55 pp. (Washington, D.C.)

Hagstrum, D. W. and M. S. Mulla. 1968. Petroleum oils as mosquito larvicides and pupicides. I. Correlation of physicochemical properties with biological activity. J. Econ. Entomol. 61:220–225.

Jarvis, N. L. and W. A. Zisman. 1966. Surface chemistry of fluorochemicals. Encyclopedia of Chemical Technology. 9:707–738. Wiley and Sons, Inc., New York.

Lorenzen, G. A. and W. W. Meinke. 1968. A feasibility study on the utilization of monomolecular films for mosquito abatement. Mosquito News 28:230–232.

Manzelli. M. A. 1941. Studies of the effect of reduction of surface tension on mosquito pupae. Proc. N. J. Mosq. Exterm. Assoc. 28:19–23.

McMullen, A. I. and M. N. Hill. 1971. Anoxia in mosquito pupae under insoluble monolayers. Nature 234:51–52.

Msangi, A. S. 1956. Cetyl alcohol and larval mosquito control. East African Med. J. 33:353–356.

Mulla, M. S. and M. F. B. Chaudhury. 1968. Effects of surface tension on pupae of *Culex pipiens quinquefasciatus* Say and *Aedes aegypti* (L.). Mosquito News 28:187–191.

Russell, P. F. and T. R. Rao. 1941. On surface tension of water in relation to behavior of *Anopheles* larvae. An. J. Trop. Med. 21:767–777.

Senior-White, R. 1943. Effect of reduction of surface tension on mosquito pupae. Indian Med. Gaz. 78:342.

Singh, K. R. P. and D. W. Micks. 1957. The effects of surface tension on mosquito development. Mosquito News 17:70–73.

Watson, G. I. 1941. A physiological study of mosquito larvae which were treated with anti-malarial oils. Bull. Entomol. Res. 31:319–330.

WHO. 1973. *Manual on larval control operations in malaria programmes.* World Health Organization. Geneva, Switzerland. pp. 88–90.

Wiltzius, W. J. 1967. Effects of monolayers on insects, fish and wildlife. Research Report 7, Bureau of Reclamation, U. S. Department of the Interior, 67 pp.

Zisman, W. A. 1964. Relation of the equilibrium contact angle to liquid and solid constitution, in *Contact Angle, Wettability and Adhesion,* ed. R. F. Gould, Advances in Chemistry Series 43. American Chemical Society. Washington, D. C. pp. 16–21.