

# Controlled-Release Herbicide-Polymer Formulations for Aquatic Weed Control

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The slow migration of polymer additives such as plasticizers and stabilizers from polymer matrices is well established (7, 9, 11). Recently this phenomenon has been utilized in development of a wide variety of controlled-release pesticide-polymer formulations. For example, the slow migration of mosquito larvicides from polyvinyl chloride (8, 13) and natural rubber (10) formulations has been used to control mosquito larvae for up to 6 months. Commercial formulations of organotin toxicants in natural rubber prevent marine fouling for at least 7 years (2).

In addition to long-term control, controlled-release formulations have several distinct advantages over other formulations. They (a) minimize pesticide residues available to the environment, (b) maintain toxic concentrations of pesticide in close proximity to the target organism, (c) increase the efficacy and longevity of the pesticide by protecting it from environmental degradation, and (d) decrease application costs because less frequent applications are required.

Limited field tests have shown that controlled-release herbicide-polymer formulations have potential value in aquatic weed control. Formulations of herbicides in polyvinyl chloride (12) and natural rubber (3) have been used to control aquatic weeds. In order for herbicide-polymer formulations to be used effectively in the future, it is important that persons active in the field of aquatic weed control be familiar with the basic concepts of controlled release. A typical release pattern for a controlled-release formulation is shown in Figure 1. This figure depicts the daily herbicide release of a 20% formulation of the sodium salt of (2,3,6-trichlorophenyl) acetic acid (fenac) in polyethylene (5). The initial peak is due to loss of herbicide on or near the surface of the formulation. The release pattern lends itself well to aquatic weed control. The relatively large initial release can be utilized to kill weeds quickly. In some instances it may be desirable to combine the application of a controlled-release formulation with a reduced conventional application of herbicide. In either case,

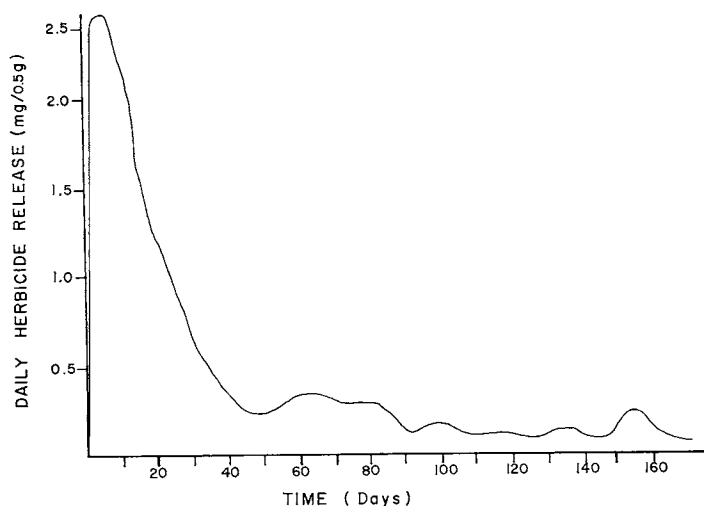


Figure 1. Daily herbicide release of a 20% formulation of the sodium salt of fenac in polyethylene (5).

the continued release of extremely small amounts of herbicide may retard regrowth.

The actual migration of the herbicide from the polymer matrix is governed by the principles that underlie the transfer of matter (4, 9). The migrating herbicide meets two resistances: (a) in moving from the interior of the matrix to the surface (diffusion), and (b) in escaping from the surface into the surrounding medium (dissolution). The rate of loss of herbicide depends on the rate at which the particular molecule overcomes these resistances. It is conceivable that both resistances might be of the same magnitude; however, all previously studied systems have fallen into one of the extreme cases where one resistance is rate-controlling (9).

When diffusion is rate-controlling, herbicide loss is proportional to the square root of time (1, 9). The mathematical expression which relates these two parameters depends on the mechanism of release and the geometry of the system. For example, two mechanisms described by different mathematical expressions have been proposed for the release of drugs from solid polymer matrices into media that act essentially as perfect sinks (6).

In the first mechanism the additive molecule is thought to diffuse through and from an enveloping, homogenous matrix (Figure 2). Higuchi (6) has proposed that the rate of release of an additive from one surface of such a matrix is governed by the following relationship:

$$Q = \sqrt{Dt(2A - C_s)C_s}$$

where  $Q$  = the amount of additive released after time  $t$  per unit exposed area,  $D$  = the diffusion coefficient of the additive in the homogenous matrix,  $A$  = the total amount of additive present in the matrix per unit volume, and  $C_s$  = the solubility of the additive in the matrix substance.

In the second mechanism the surrounding medium is thought to enter the matrix through pores, cracks, and intergranular spaces (Figure 2). The additive is presumed to dissolve slowly into the permeating fluid phase and to

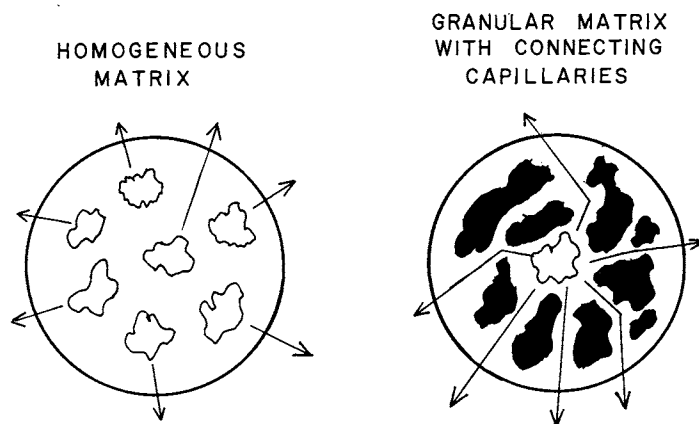


Figure 2. Two mechanisms of herbicide release from a polymer matrix.

diffuse from the system along the cracks and capillary channels filled with the extracting solvent. For this system Higuchi (6) derived the relationship:

$$Q = \sqrt{\frac{D\epsilon}{\tau}(2A - \epsilon C_s) C_s t}$$

where  $Q$  = the amount of additive released after time  $t$  per unit exposed area,  $D$  = the diffusion coefficient of additive in the release medium,  $\epsilon$  = the porosity of the matrix,  $\tau$  = the tortuosity of the capillary system (corrects for the lengthened diffusional path caused by lateral excursions),  $A$  = the total amount of additive present in the matrix per unit volume, and  $C_s$  = the solubility of the additive in the surrounding medium.

Surface resistance (dissolution) is rate-controlling if the resistance to loss from the surface of the matrix is high compared to the resistance of the matrix itself. Within this condition, surface resistance may vary, depending on: (a) a driving potential (for loss of herbicide into water this driving potential is the difference between the solubility of the herbicide in water and the concentration of herbicide in the water surrounding the sample), and (b) the state of turbulence of the medium, which is governed by its velocity, density, and viscosity.

When surface resistance is rate-controlling, the system follows first order kinetics and herbicide loss is proportional to time according to the following equation (7, 9):

$$Q = A(1 - e^{-kt})$$

where  $Q$  = the amount of herbicide released after time  $t$  per unit exposed area,  $A$  = the amount of herbicide in the matrix per unit volume,  $k$  = the rate loss constant, and  $e$  = the base of natural logarithms.

The rate-controlling step in herbicide release then must be determined for each new herbicide-polymer formulation. In cases where herbicide loss is controlled by dissolution, the aquatic turbulence and the solubility of the herbicide in the water to be treated will be the major factors in determining the release rate. In cases where herbicide loss is controlled by diffusion, the factors that determine the release rate will depend on the mechanism of release. Formulations of this type, however, are highly desirable

as proper choice of the variable factors in their preparation should allow one to "custom formulate" a product with a desired release rate.

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