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As the world's population rapidly increases, agriculture is faced with the demand for enhanced production utilizing chemicals with little or no detrimental effect on the surrounding environment. Pesticide leaching into drainage waters and subsequent transport into non-target areas is of growing ecological concern. The immensity of the problem is apparent when considering the total agricultural pesticide application and the annual run-off for drainage areas.

The Mississippi Watershed area alone covers 1,244,000 square miles including vast stretches of central U.S. farmland. The annual water discharge at the mouth of the Mississippi has been estimated to 7.8×10^{11} yds³ and 2,000,000 tons of sediment are carried into the sea per day. The average annual rainfall over this area is about 30 inches, of which about one-fourth travels to the Gulf of Mexico by way of the Mississippi River (1,2).

In 1974, nearly 1.4 billion pounds of organic pesticides were sold by U.S. companies, representing a growth of 12% over 1973. Insecticides accounted for 50.4% of the total volume with the balance consisting of herbicides, fungicides, and plant hormones (3). With some pesticide systems, 70 - 80% of the useful chemical activity is lost by various mechanisms including interaction with non-target organisms. Scientists have measured the rates of loss of activity of various chemicals in terms of "persistence" levels. Persistent pesticides have been attacked in environmental studies due to their usual migration to non-target areas. However, it should be pointed out that some degree of persistence is necessary to yield weed, insect or fungus control for a reasonable period of time in the target area. Often the most persistent chemicals are also the most effective.

Several factors are known to determine persistence in the soil. These include (a) uptake and degradation by microorganisms, (b) loss through physical processes of volatilization and leaching, and (c) chemical changes such as photo-decomposition and chemical reactions (4).

The Environmental Protection Agency is imposing stringent requirements on several effective and previously widely used pesticides. The type, amount applied, specificity, and persistence of each pesticide will be under continuing scrutiny. The pest control agents must not merely control target organisms but must be harmless to humans, livestock, crops, fish, wildlife, beneficial insects, soil microorganisms, etc.

Dramatic improvements in analytical instrumentation have allowed claims of detection of trace amounts of organic chemicals in non-target areas in the parts per billion range. This advance, in conjunction with the controversy generated by adverse publicity on insecticides such as DDT and Mirex, has led to a flurry of experiments on nearly every chemical manufactured in the U.S. Particular emphasis has been placed on chemicals having potential impact on the aquatic environment. For example, Cutler (5-12) has reported growing evidence that "the continuing use of pesticide chemicals is producing environmental changes or residues in the food web that may cause reproductive failure. . ." Some organisms have been shown to accumulate or concentrate certain persistent pesticides at alarming rates. The oyster, for example, when continuously exposed to 0.1 ppb of DDT, was reported to concentrate in its tissues up to 7.0 ppm in a month. It may be predicted that chlorinated herbicides will soon come under attack (13, 28-30).

Stringent rules and regulations (apparently subject to frequent modification) have been imposed on agricultural chemical producers and consumers as a result of environmental studies. Many knowledgeable sources predict an impending disaster for the whole agricultural industry from the high costs of licensing, registration, and production of new pesticides. In 1976, new pesticide commercialization required an average of 2.5 years of research and development at a cost of over \$10,000,000.00. The agricultural industry has, in general, responded to the environmental regulations by producing less persistent but often less effective pesticides, requiring more frequent application over an extended growing season. A more logical and certainly more fruitful approach is to attack the undesired "leaching" or transport of a given pesticide rather than its "persistence."

Agricultural chemical leaching and subsequent pesticide transport to non-target environments can be greatly reduced, possibly eliminated, by controlled-release systems based on macromolecules. Polymers can be synthesized which contain reactive chemical bonds to common pesticides; these bonds are subject to enzymatic or hydrolytic break-down at a controllable rate. The macromolecular nature of these systems will prevent dissolution, leaching and transport to non-target areas. Controlled-release can also reduce the number of applications and the quantity of chemical required for pest control. A number of naturally occurring polymers (25-27) offer excellent potential as raw materials for substrate preparation of controlled release systems. In addition, certain polysaccharides decompose yielding

products beneficial to the soil.

Development of a commercial herbicide system must combine effectiveness, favorable economics, with little adverse environmental impact. The chemical must: (1) control weeds at reasonable dosages, (2) selectively control target organisms only, leaving beneficial insects, plants, and humans unharmed, (3) persist for a reasonable time, (4) be inexpensive for large scale usage, and (5) and be easily applied, (preferably with conventional equipment).

Provided the above criteria are met, potential benefits derived from properly formulated controlled-release systems include: (1) enhanced agricultural production, (2) fewer applications, (3) less environmental pollution and (4) reduced production costs to the farmer.

Macromolecular Design

Polymeric systems for controlled-release of pesticides may be assigned to two broad categories. In the first, the pesticide is physically dissolved, entrapped, or dispersed in a polymer matrix. Chemical release is generally based on diffusion phenomena (14-19, 34-39); however, chemical or biological erosion of the polymer matrix is also possible. In the second category, the pesticide is chemically bound (pendant) to the macromolecular backbone. Release is then dependent on the rate of chemical or biological break-down of the polymer-to-pesticide bonds (20-24, 31-39).

Polymers containing pendant pesticides can be prepared by two synthetic methods. The first involves bonding (via covalent or ionic chemical bonds) of a pesticide to a pre-formed polymer. This approach requires macromolecules with pendant functional groups capable of reaction with pesticides or their derivatives. The nature of the chemical bond may be varied to yield bonds with quite different rates of cleavage in the environment. Advantages of this method include: (a) availability of relatively inexpensive polymers with biodegradability such as chitin, cellulose, etc., and (b) use of commercially available pesticides as starting materials in polymer synthesis.

The second approach involves polymerization of monomeric pesticides. The major advantages of this method lie in the ability to control the molecular design of the polymer and the pesticide/polymer weight ratio.

Experimental

Preformed, hydroxy-containing polymers were selected for initial study. Three polymers - polyvinyl alcohol, chitin, and cellulose were chosen on the basis of: (a) potential biodegradability, (b) commercial availability, and (c) hydrophilicity in addition to having proper pendant functionality. The results of the experiments on polyvinyl alcohol are reported in this work.

Metribuzin was chosen as a model pesticide based on: (a) available amine functionality, (b) high activity at relatively low concentrations, (c) selectivity, (d) lack of persistence in the environment, and (e) high mobility.

A series of laboratory and commercial polymers of polyvinyl alcohol (with varying residual amounts of unhydrolyzed vinyl acetate) were carefully characterized. Isocyanate adducts of metribuzin were prepared and reacted with the pendant hydroxyl functionality of the pre-formed polymers (Figure 1). It was possible to prepare copolymers with varying degrees of substitution on linear and highly cross-linked chains.

The isocyanate to hydroxyl ratios were varied over a wide range to prepare solvent swollen, cross-linked gels. These were converted to microporous solids by agitation of the product in the presence of a non-solvent (selected from solubility parameter data).

Rates of Release of Metribuzin

Polymers with pendant metribuzin (0.100 g) were placed in an Erlenmeyer flask. 500 ml of distilled water was added. At designated intervals, samples were taken to determine the concentration of released metribuzin.

Ultraviolet Spectroscopic Method. A Cary 1756 Spectrophotometer was used to determine released metribuzin levels in water. A standard plot of absorbance vs. concentration was obtained using least squares analysis. 3 ml samples were taken at designated intervals and placed in standard quartz cells. The absorbance at 293.5 nm was monitored in two types of tests. The first measured total concentration of released metribuzin over a time period. The second test was conducted as follows: (a) 0.100 g samples were placed in 500 ml of distilled water for a predetermined time; (b) the samples were filtered, dried and again placed in a second Erlenmeyer flask containing 500 ml of distilled water; (c) concentrations were measured directly from the filtrate.

Gas Chromatographic Method. 2 μ l of aqueous solution were removed and extracted with 5.0 ml of benzene. 1 μ l of the benzene phase was then injected into the gas chromatograph (Micro-Tek 220 with electron capture detector).

Soil Mobility Studies

Thin-layer plates were prepared by spreading a soil slurry onto 20 X 20 cm glass plates to a thickness of 1.0 mm. Plates were divided into three equal sections by scribing the soil layer. Metribuzin was applied to one plate by streaking 500 λ of a 100 g/ml solution onto each section of the plate 2 cm from the bottom. Polymers containing pendant metribuzin were embedded in

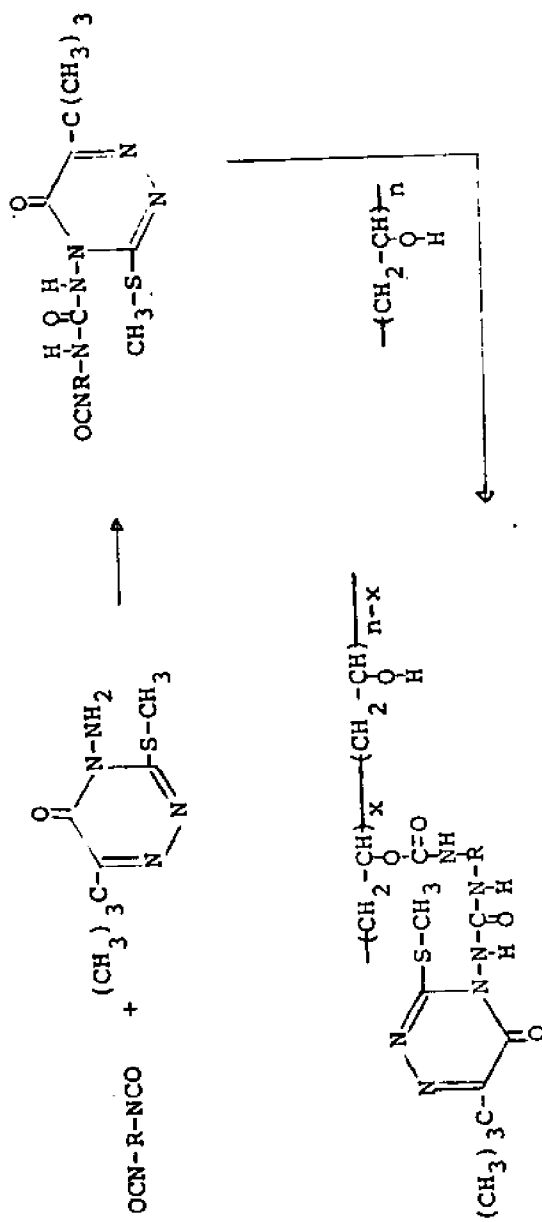


Figure 1. Synthetic method for preparation of PVA copolymer containing pendant metribuzin

the soil layer on other plates which were also divided into three sections. The plates were eluted to 10 cm with water, air dried, and 1-cm zones were removed from one of the three sections of each plate. The plates were returned to the chamber and again eluted with 10 cm of water, and the second zone was removed in 1-cm sections. This procedure was repeated with the third section of soil. The soil removed in this manner was extracted with 5 ml of hexane: acetone (3:1) by shaking. Extract was analyzed by gas chromatography.

Residual Phytotoxicity Of Metribuzin From Polymers

The polymers containing pendant metribuzin were added to the surface of a Bosket sandy loam soil contained in 4" plastic pots in a controlled-environment chamber. The application rates were 0, 0.1, 0.2, and 0.3 g of each formulation. A commercial formulation of metribuzin was applied to other pots at 0.5 and 1.0 ppmw, and thoroughly mixed into the soil. The soils were bioassayed over a period of 112 days with a mixture of weeds which are normally susceptible to the herbicide; after growing two weeks, the weeds were harvested and first weights recorded.

Results And Discussion

Five polymers containing pendant metribuzin were chosen for study: 22-S, 23-S, 41-S, 45-S, and 50-S. 23-S, 45-S, and 50-S were essentially linear polymers prepared from 99% hydrolyzed polyvinyl alcohol. 22-S and 41-S were highly cross-linked microporous solids. These system require both hydrolysis of the urea bond and diffusion from a water swollen, cross-linked matrix for metribuzin release.

Plots of solution concentration vs. time (Figures 2, 3) indicated that the linear polymers (23-S, 45-S, and 50-S) released herbicide much more rapidly than the cross-linked systems. The 23-S, 45-S, and 50-S were characterized by a rapid initial release in the first few hours followed by a more gradual rate lasting several days. The cross-linked systems 22-S and 41-S (Figure 4) had much lower release rates with little initial release. This could be predicted by the time required for swelling of the hydrophilic polymer so that hydrolysis and diffusion could occur. After swelling, slight concentration increases were noted. The u.v. spectroscopic data and the gas chromatographic data were internally consistent. It should be noted that the ultraviolet technique requires no extraction and, therefore, offers less chance for error at small concentrations of metribuzin.

Soil thin-layer chromatographic techniques showed metribuzin (Figure 5) moved as a normal chromatogram peak with each successive elution moving the peak nearer the 10-cm zone. The chromatograms from 23-S (Figure 6) and 45-S (Figure 7) showed "streaking" continuously along the plate indicating a sustained release mechanism. The cross-linked formulations, 22-S and 45-S,

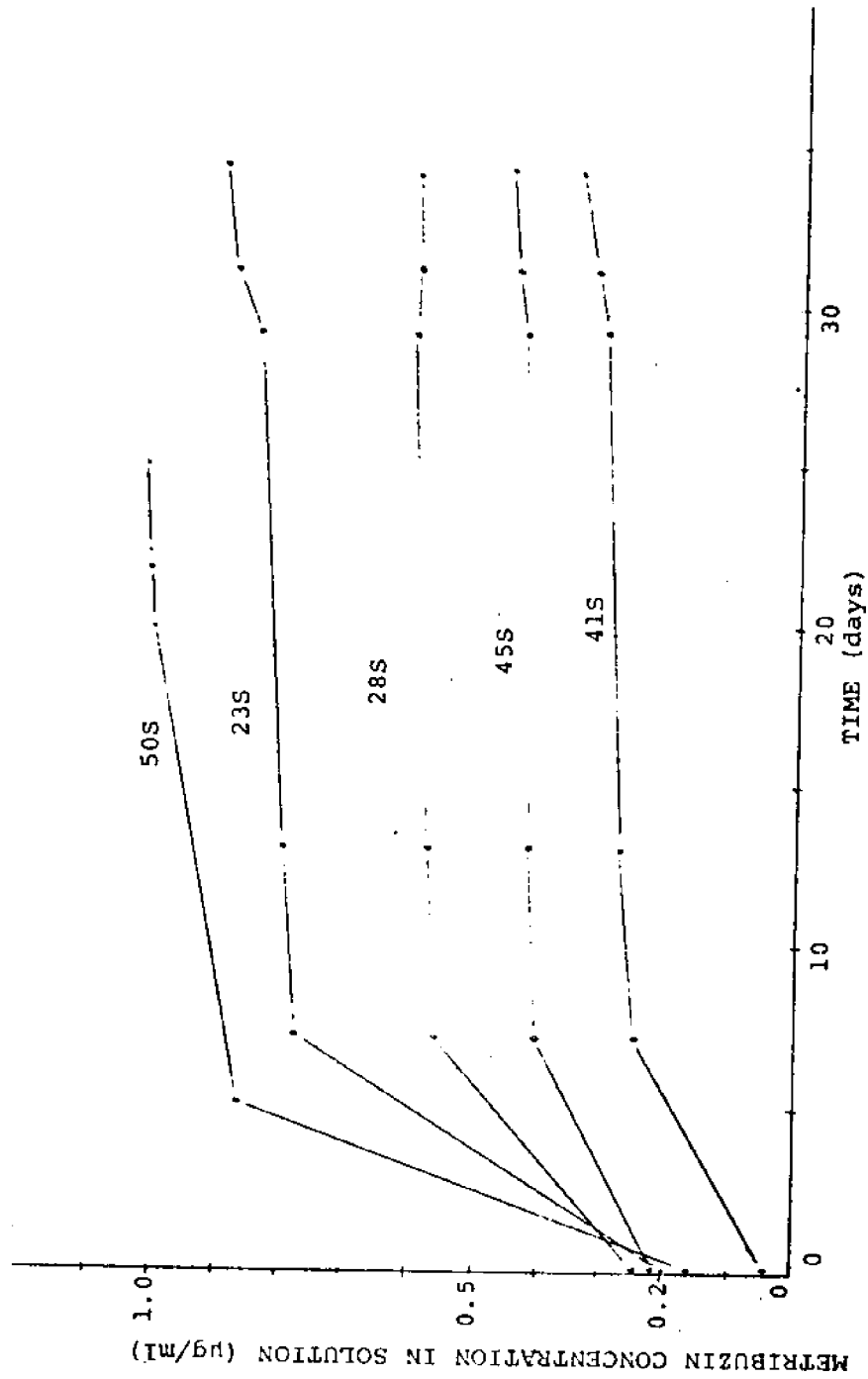


Figure 2. Metribuzin release from polymers in water (ultraviolet spectroscopy)

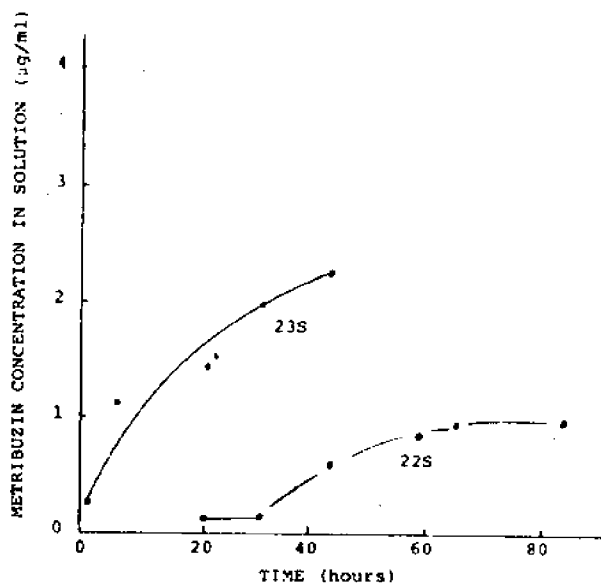


Figure 3. Metribuzin release from linear (23S) and cross-linked (22S) polymers

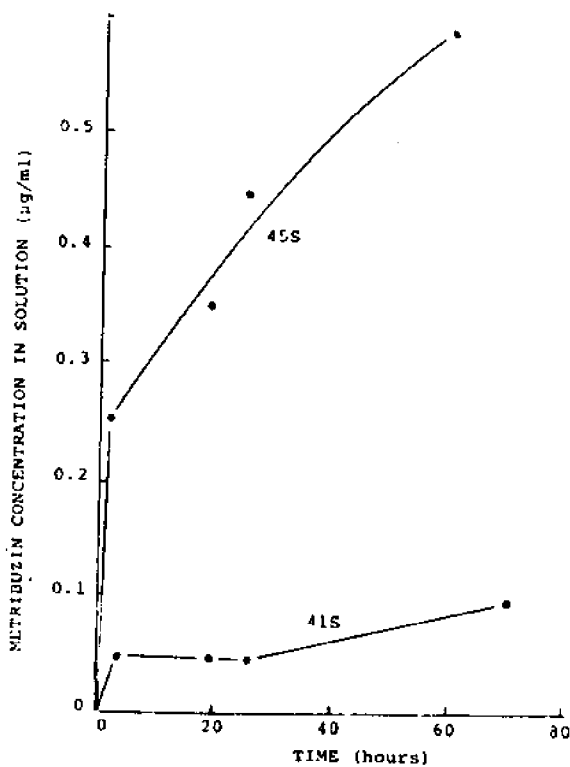


Figure 4. Metribuzin release from linear (45S) and cross-linked (41S) polymers

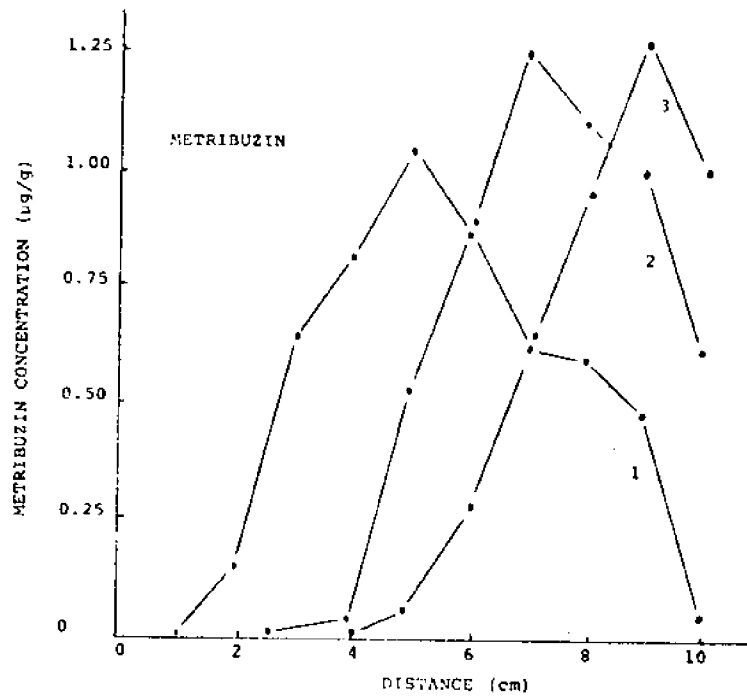


Figure 5. Soil thin layer chromatography (TLC) of metribuzin

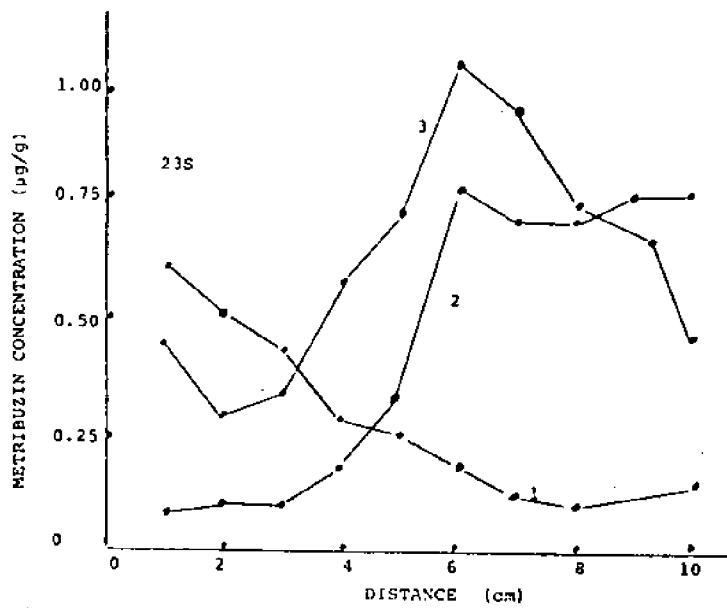


Figure 6. Soil TLC of metribuzin released from 23S

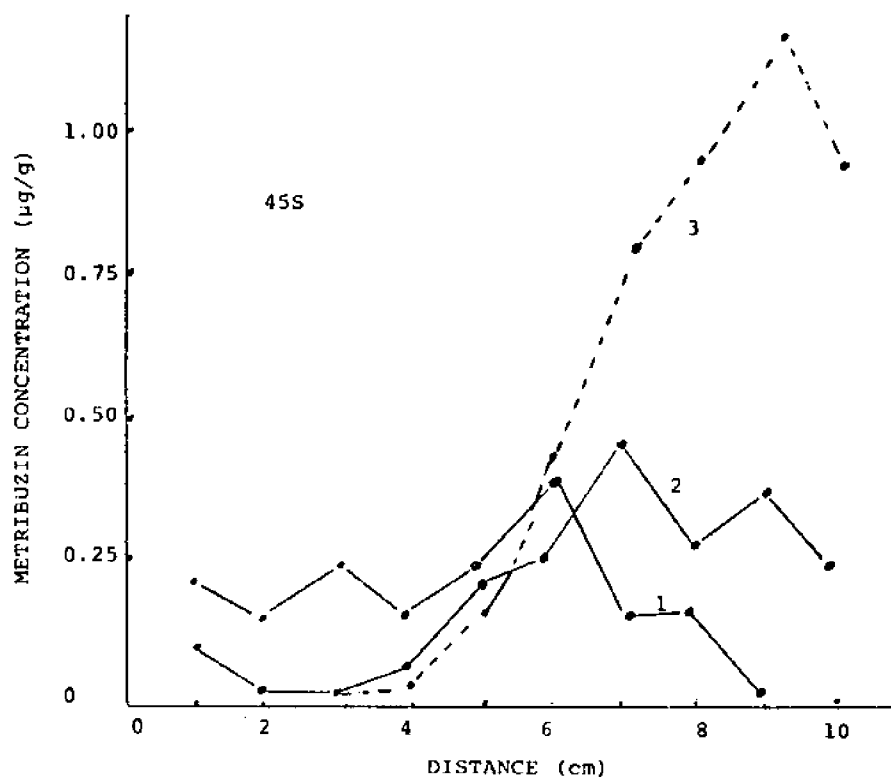


Figure 7. Soil TLC of metribuzin released from 45S

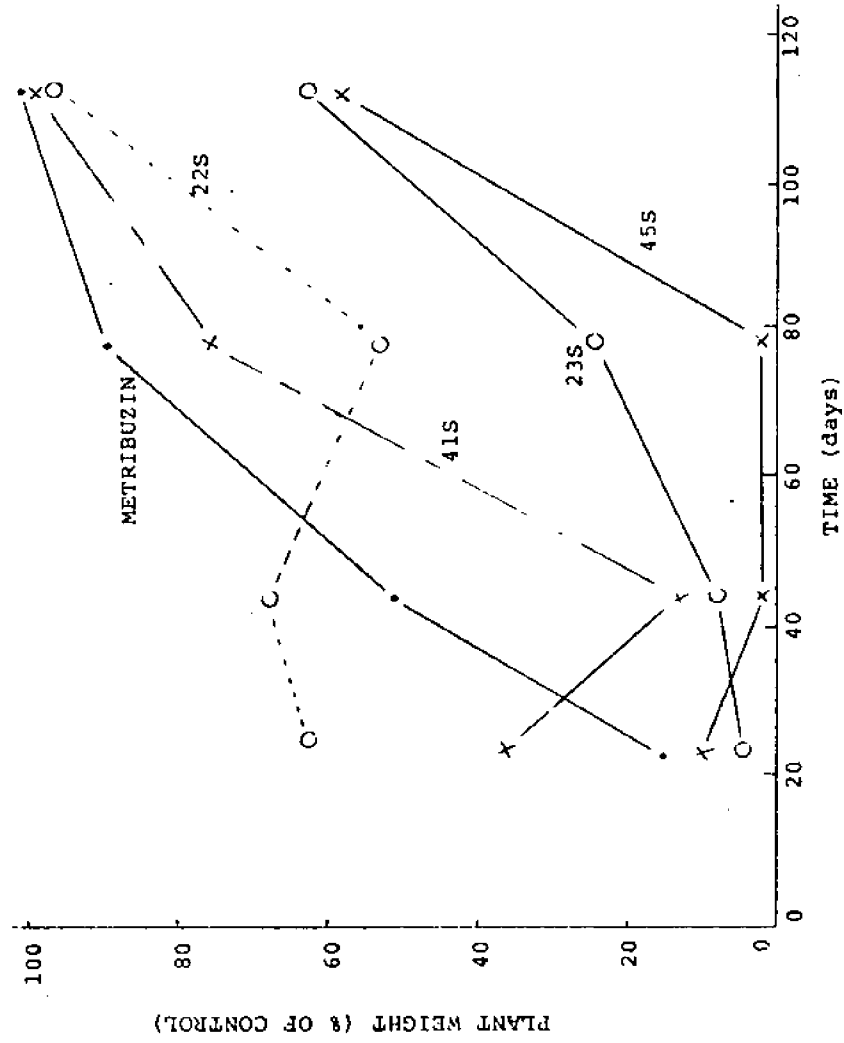


Figure 8. Phytotoxicity of metribuzin from polymer formulations as a function of time

did not release enough metribuzin for a measurable rate in these studies.

Residual phytotoxicity of the four polymeric systems is illustrated in Figure 8. Metribuzin at 1.0 ppmw had dissipated to a level which was essentially non-toxic after 78 days. Likewise, phytotoxicity from 41-S had diminished to a large extent by this time. A relatively low level of phytotoxicity was observed for 22-S initially; however, this same level was maintained for over 78 days, then rapidly decreased.

The highest level of phytotoxicity was observed with 23-S and 45-S. These materials were still showing phytotoxicity at our last test date of 112 days.

It must be noted that phytotoxicity comparison tests of polymeric controlled-release formulations and commercially formulated herbicides must be interpreted with care. In the pendant polymeric systems, herbicides are not phytotoxic until bond cleavage has occurred. For this reason the total herbicide eventually available in the polymer cannot be compared to that immediately available in a commercial formulation.

Conclusions

Polymeric systems for controlled release of metribuzin have been prepared using biodegradable substrates. Properly selected macromolecular substrates were reacted with pesticide adducts to yield systems with labile pesticide-to-polymer bonds susceptible to chemical or enzymatic hydrolysis.

The metribuzin/polyvinyl alcohol system in this work is adaptable for formation of a range of products with different degrees of cross-linking and, therefore, different rates of herbicide release. Phytotoxicity, soil thin-layer chromatography, ultraviolet spectroscopy, and gas chromatography tests showed sustained release capabilities of the polymeric systems.

The preliminary results of this research point to the immense potential of polymeric systems for controlled-release of selective herbicides which can: (1) reduce environmental pollution in non-target areas by reducing pesticide mobility, (2) require fewer applications during the growing season, and (3) result in enhanced agricultural production at, perhaps, lower cost to the farmer.

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Abstract

Recently, there has been a growing interest in developing pesticide controlled release technology. Much of the impetus has resulted from demands for enhanced agricultural production at lower levels of environmental risk. Most of the activity has been directed toward formulations in which the pesticide is physically dissolved or dispersed in a polymer matrix. Polymers have been prepared in our laboratories which contain labile polymer to pesticide covalent bonds. These linkages are susceptible to aqueous and/or bacterial break-down, resulting in long-term release. Theoretically, the rate of herbicide release can be controlled by changing the nature of the labile bonds or by altering the cross-link density of the polymer. The synthesized systems have been characterized by IR, NMR, U.V., GPC, etc. Release studies have been conducted in aqueous media using U.V. and gas chromatography. In addition, soil mobility and phytotoxicity studies are in progress.

Literature Cited

1. Barrett, B. B., Louisiana Wildlife and Fisheries Commission Report, Cooperative Gulf of Mexico Estuarine Inventory and Study, Hydrology, p. 115, 1971.
2. Christmas, J.Y., Ed., Cooperative Gulf of Mexico Estuarine Inventory and Study, Mississippi, Publishers: Gulf Coast Research Laboratory, p. 12, 1973.
3. Chemical and Engineering News, July 28, 1975, pp. 18-31.
4. Kearney, R.C. and Kaufman, D.D., Herbicides, Chemistry, Degradation, and Mode of Action, 2nd Edition, Marcel Dekker, Inc., 1975.
5. Butler, P.A., Pesticide Monitoring Journal, Vol. 6(4) 238, 1973.
6. Butler, P.A., "Pesticides in the Estuary," Proc. of Marsh and Estuary Management Symposium (July 1967), Baton Rouge, LA, pp. 120-124, 1968.
7. Butler, P.A., Proc. of National Symposium on Estuarine Pollution, (August, 1967) Stanford University, p. 107, 1968.
8. Butler, P.A., "Significance of DDT Residue in Estuarine Fauna," Chemical Fallout, Chapter 9, pp. 205-220, 1969.
9. "Pesticides in the Marine Environment," Journal Appl. Ecology 3, (Supplement) pp. 253-259, 1966.
10. "Problems of Pesticides in Estuaries," American Fish Soc., SPE Public No. 3, pp. 110-115, 1966.
11. Firth, F.E., Ed., "Pesticides in the Sea," Encyclopedia of Marine Resources, pp. 513-516.
12. Butler, P.A., "Pesticides," U.S. Bureau of Commercial Fisheries Report: Contract No. 85, 1967.

13. Andus, L.J., Ed., The Physiology and Biochemistry of Herbicides, Academic Press, New York, 1964.
14. U.S. Patent #3,074,845.
15. U.S. Patent #3,318,769.
16. U.S. Patent #3,737,521.
17. U.S. Patent #3,127,752.
18. U.S. Patent #3,400,093.
19. U.S. Patent #3,343,941.
20. Allan, G.C., et al. Nature, 234, 349 (1971).
21. Neogi, A.N., Ph.D., Thesis University of Washington, Seattle, Washington, (1970).
22. Jakube, H.D., Busch, E., F. Chem, 13 (3), p. 105 (1973).
23. Allan, G.C., et al. Int. Pest Control, 14 (2), p. 15 (1972).
24. Harris, F.W. and Post, L.K., Polymer Preprints, 16 (1), pp. 622-627, (1975).
25. Pariser, E.R. and Block, S., Chitin and Chitin Derivatives, Report No. MITSG 73-2, October 15, 1972, (A bibliography with 593 references).
26. Davidson, R.L. and Sittig, Marshall, Eds., Water-Soluble Resins, Van Nostrand Reinhold Co., New York, 1968.
27. Bikales, N.M., Water-Soluble Polymers, Plenum Press, New York, 1973.
28. O'Brien, R.D., Insecticides, Action and Metabolism, Academic Press, New York, 1967.
29. White-Stevens, R., Pesticides in the Environment, Marcel Dekker, 1973.
30. Chemical Engineering, January 19, 1976.
31. Allan, G.C., Canadian Patent #846785.
32. Allan, G.C., Canadian Patent #863310.
33. Allan, G.C., Canadian Patent #855181.
34. Chemical and Engineering News, June 28, 1976.
35. Controlled Release Pesticide Symposium, The University of Akron, September, 1974.
36. Proceedings 1975 International Controlled Release Pesticide Symposium, Wright State University, September, 1975.
37. Proceedings 1976 Controlled Release Pesticide Symposium, The University of Akron, September, 1976.
38. Cardarelli, N., Controlled Release Pesticides Formulations, CRC Press, Cleveland, Ohio, 1976.
39. Paul, D.R. and Harris, F.W., Eds., Controlled Release Polymeric Formulations, ACS Symposium Series; 33, 1976.

