

DEVELOPMENT OF CONTROLLED-RELEASE POLYMER SYSTEMS CONTAINING
PENDANT METRIBUZIN

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ABSTRACT

Recently, there has been a growing interest in developing technology for controlled release of pesticides. Much of the impetus has resulted from demands for enhanced agricultural production with greater efficiency and lower levels of environmental risk. Most of the activity has been directed toward formulations in which the herbicide is physically dissolved or dispersed in a polymer matrix. Polymers have been prepared in our laboratories which contain labile covalent bonds of the polymer to metribuzin [4-amino-6-*tert*-butyl-3-(methylthio)-*as*-triazin-5(4H)-one]. These linkages are susceptible to aqueous and/or bacterial break-down resulting in release of the herbicide into the biosphere. Solution studies indicated more rapid rates of herbicide release from linear than from cross-linked polymer systems. This difference was also apparent in soil thin-layer mobility studies. Linear systems exhibited a definite release mechanism as compared to metribuzin alone. The cross-linked systems failed to release a measurable quantity of the herbicide in this system. Phytotoxicity studies verified that the parent herbicide was being released. Increased residual phytotoxicity resulted from use of these linear polymer systems containing pendant metribuzin.

INTRODUCTION

Herbicides have been used extensively for several years in the commercial production of agronomic and horticultural crops. The use of these chemicals is essential for adequate production of food and fiber crops in the United States. An effective herbicide should control weeds at reasonable doses while remaining selectively non-phytotoxic to the crop, remain in the area where applied, persist throughout the growing season, and then dissipate rapidly. Some potentially useful compounds have not been completely successful due to problems associated with selectivity, persistence, or mobility.

Systems capable of releasing a herbicide to the desired site at a controlled rate offer the potential of overcoming some of these problems and of allowing more efficient utilization of existing herbicides. Effective controlled release formulations of herbicides should allow extended periods

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of activity, while minimizing adverse environmental effects related to movement of the herbicide from the application site. Polymeric systems for controlled release of herbicide may be assigned to two broad categories. In the first, the herbicide is physically dissolved, entrapped, or dispersed in a polymer matrix. Release is generally based on diffusion phenomena (4-9, 10-25); however, chemical or biological erosion of the polymer matrix is also possible. In the second category, the herbicide is chemically bound (pendant) to the macromolecular backbone. These bonds are subject to enzymatic or hydrolytic break-down at a controllable rate.

Polymers containing pendant herbicides can be prepared by two synthetic methods. The first involves bonding (via covalent or ionic chemical bonds) of a herbicide to a pre-formed polymer. This approach requires macromolecules with pendant functional groups capable of reaction with herbicides or their derivatives. The nature of the chemical bond may be varied to yield bonds with quite different rates of cleavage in the environment. The major advantage of this method is the availability of relatively inexpensive, biodegradable polymers such as chitin, starch, cellulose, etc,

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.

Metribuzin [4-amino-6-tert-butyl-3-(methylthio)-as-triazin-5(4H)-one] is a relatively new herbicide which has been used extensively for weed control in soybeans and has proven effective on some of the more difficult weeds of the Southeast and Midwest. It is recognized that metribuzin could be a more effective herbicide if certain problems associated with its use could be overcome. Metribuzin degrades rapidly in soil (1-3). This is beneficial from an environmental pollution standpoint, but is detrimental to effective weed control, since the herbicide does not have full-season activity. Also, the herbicide is relatively phytotoxic, and even though relatively selective to soybeans, selection of the correct rate for a particular soil type is critical as soybean injury often occurs. Metribuzin is relatively soluble (1200 ppm in water) and is subject to vertical movement in the soil profile as well as lateral movement during run-off events.

Metribuzin is a herbicide which could be greatly improved by formulation into a controlled release system. Herbicide effectiveness could be enhanced by extending the period of herbicidal activity, while allowing greater crop safety and less potential for movement of the herbicides to other areas of the environment.

The objectives of this research were to synthesize polymer systems containing pendant metribuzin and to evaluate these materials as related to rates of release, mobility, and residual phytotoxicity of metribuzin.

EXPERIMENTAL

Macromolecular Synthesis.

Homopolymers of polyvinyl alcohol and copolymers of polyvinyl alcohol and polyvinyl acetate were chosen as substrates for the initial studies.

Residual Phytotoxicity Studies.

The polymers containing pendant metribuzin were added to the surface of a Bosket sandy loam soil contained in 10-cm plastic pots in a controlled-environment chamber with 14 hour photoperiod and temperatures of 30°C. 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 four times over a period of 112 days with a mixture of weeds which are normally susceptible to the herbicide. Plants were grown for 2 weeks, harvested, and fresh weights were recorded. Data were expressed as percent of the untreated control.

RESULTS AND DISCUSSION

Plots of solution concentration vs. time (Figures 2 and 3) indicated that the linear polymer systems (23-S and 45-S) released herbicide much more rapidly than the cross-linked systems (22-S and 41-S). The 23-S and 45-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 system 22-S and 41-S (Figures 2 and 3) had much lower release rates with little initial release. This slower release is likely due to the time required for swelling of the hydrophilic polymer so that hydrolysis and diffusion can occur. After swelling, slight concentration increases were noted. Results from the two experiments were comparable.

Soil thin-layer chromatographic techniques showed metribuzin (Figure 4) moved as a normal chromatogram with each successive elution moving the peak nearer the 10-cm zone. The chromatograms from 23-S (Figure 5) and 45-S (Figure 6) showed a much different mobility pattern. Metribuzin was released from 23-S at a definite rate in the initial elution resulting in a "streaking" effect on the chromatogram. Succeeding elution resulted in the movement of this free metribuzin in a manner similar to that observed in Figure 4; however, the zone near the origin of the chromatogram still indicates that more metribuzin is being released from the polymer system. The other linear polymer system, 45-S, indicated a release similar to 23-S in the initial elution followed by normal movement of the free metribuzin in subsequent elutions. Some indication of further release is given by continued "streaking" of the metribuzin in the second elution. The mobility pattern in the third elution indicates little release is occurring. A release mechanism is obviously present in these linear polymer formulations of metribuzin, resulting in restricted mobility of metribuzin. Sustained release is not strongly apparent in these systems, probably due to the short time interval represented by the three elutions. Very little time was available for hydrolysis reaction which would be necessary for metribuzin release.

The cross-linked formulations, 22-S and 41-S, did not release enough metribuzin to be measurable in the soil thin-layer system.

These polymers are commercially available, biodegradable, and hydrophilic. The extent of hydroxyl functionality is easily controlled by varying the residual amounts of unhydrolyzed polyvinylacetate. After molecular characterization, the polyvinyl alcohol copolymers were reacted with isocyanate adducts of metribuzin (Figure 1). The isocyanate to hydroxyl ratios were varied over wide ranges to prepare a variety of pendantly substituted polymers. Linear (23-S and 45-S) polymer systems were prepared from 99% hydrolyzed polyvinyl alcohol. Moderately (41-S) to highly (22-S) cross-linked polymer systems were prepared and isolated by precipitation from non solvents. These cross-linked systems require both hydrolysis of the urea bond and diffusion from a water-swollen, cross-linked matrix for metribuzin release.

Rates of Release of Metribuzin.

Experiment 1. Samples (0.100 g) of polymers with pendant metribuzin were placed in an Erlenmeyer flask with 500 ml of distilled water and stirred. At designated intervals the solutions were subsampled and metribuzin content was determined by ultraviolet spectroscopy at 293.5 nm.

Experiment 2. Samples (0.100 g) of polymers with pendant metribuzin were placed in a flask with 500 ml of distilled water and stirred for 80 hours. At designated time intervals stirring was halted long enough to withdraw 2-ml aliquots of the supernatant. These aqueous samples were extracted with 5 ml of benzene and 1- μ l aliquots of the benzene phase were injected into a gas chromatograph equipped with a ^{63}Ni electron capture detector and a 6-mm i.d. x 1.8-m glass column packed with 3% OV-1 on 80-100 mesh Chromosorb W⁴. Inlet, column, and detector temperature were 210, 185, and 225°C, respectively. Sensitivity was 0.015 $\mu\text{g}/\text{ml}$, with linear response up to 0.25 $\mu\text{g}/\text{ml}$.

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 μl of a 100 $\mu\text{g}/\text{ml}$ solution onto each section of the plate 2 cm from the bottom. Polymers containing pendant metribuzin were embedded in the soil layer on other plates which were also divided into three sections. The plates were developed 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, again developed to 10 cm with water, and the second zone was removed in 1-cm sections. This procedure was repeated with the third zone of soil. The soil removed in this manner was extracted by shaking with 5 ml of hexane:acetone (3:1). Extracts were analyzed by gas chromatography as described previously.

⁴Mention of a trademark or proprietary product does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval to the exclusion of other products that may also be suitable.

Residual phytotoxicity of the four polymeric systems is illustrated in Figure 7. Metribuzin at 1.0 ppmw had dissipated to a level which was essentially non-toxic after 78 days. Phytotoxicity from 41-S increased from 20 to 44 days, then diminished rapidly to 78 days. A relatively low level of phytotoxicity was observed for 22-S initially; however, this same level was maintained for 78 days, then rapidly decreased.

The highest level of phytotoxicity was observed with 23-S and 45-S, indicating a rapid initial release rate of metribuzin. Evidently these materials were releasing metribuzin during the study since phytotoxicity remained high at 78 days, and was also apparent at our last test date of 112 days.

Phytotoxicity comparison tests of polymeric controlled-release herbicide 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 applied in the polymer system, which is eventually available but is not directly comparable to the total amount of herbicide applied as a commercial formulation. In controlled-release systems release rate largely determines effective dosage, while total herbicide content largely determines duration of activity.

SUMMARY AND CONCLUSIONS

Polymeric systems for controlled release of metribuzin have been prepared using biodegradable substrates. Properly substituted macromolecular substrates were reacted with metribuzin adducts to yield systems with labile herbicide-to-polymer bonds which are susceptible to chemical or enzymatic hydrolysis. The metribuzin/polyvinyl alcohol system in this work is adaptable for the formulation of a range of products with different degrees of cross-linking and, therefore, different rates of herbicide release. Phytotoxicity, soil thin-layer chromatography, and solution studies showed sustained release capabilities of the polymeric systems with practical implication toward reducing metribuzin mobility in soil and increasing residual phytotoxicity.

ACKNOWLEDGMENTS

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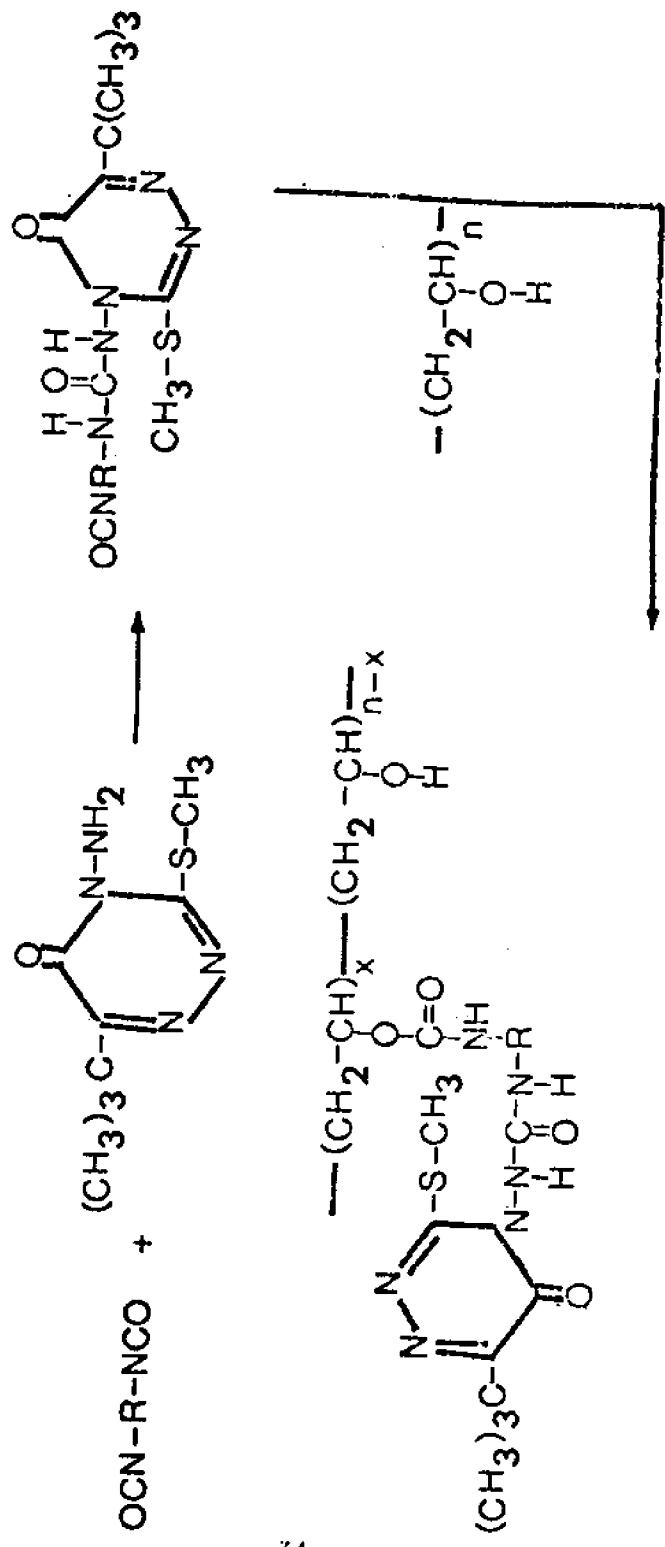


Figure 1. Schematic synthesis of polymer system containing pendant metribuzin.

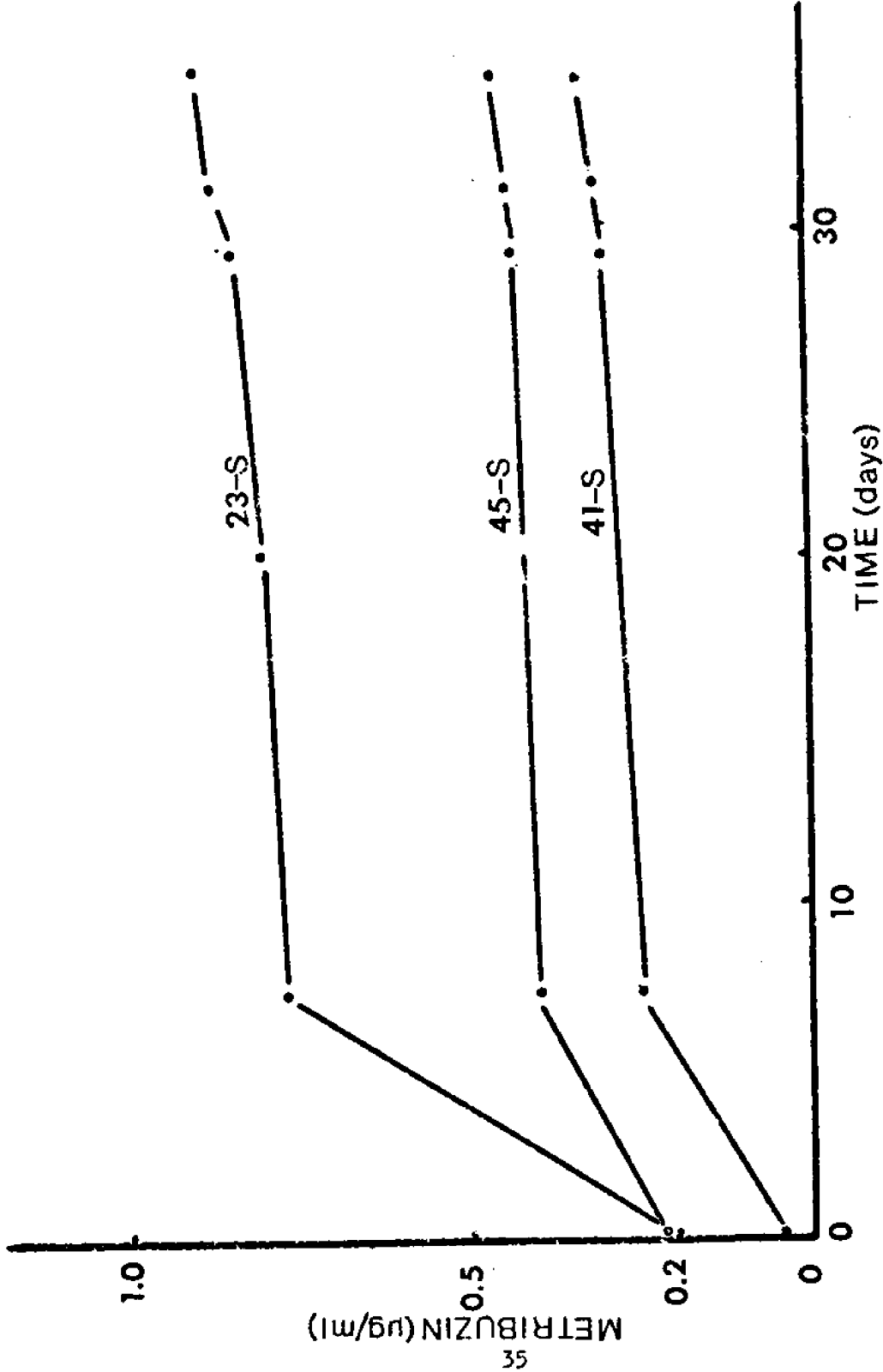


Figure 2. Release of metribuzin from 23-S, 45-S, and 41-S in aqueous systems as monitored by ultraviolet spectroscopy.

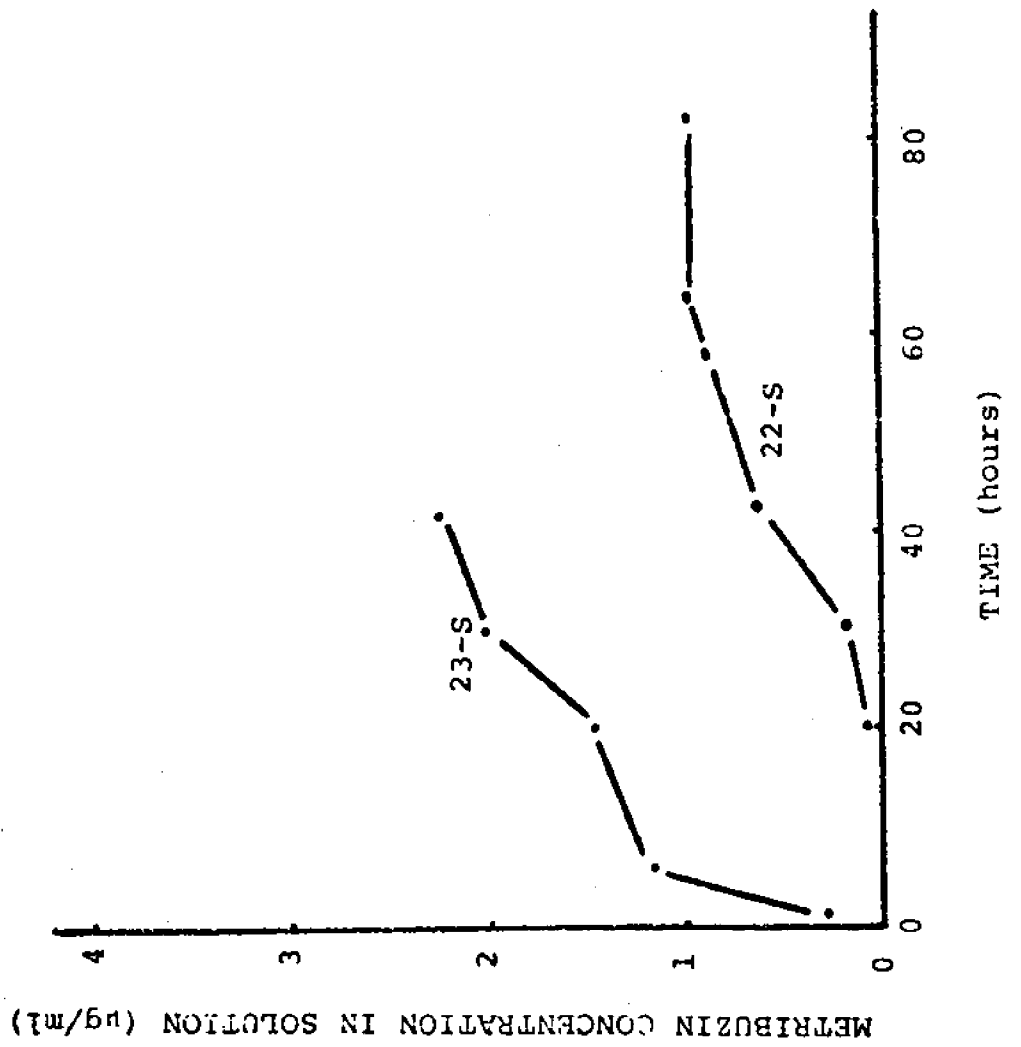


Figure 3. Release of metribuzin from 23-S and 22-S in aqueous systems as monitored by gas chromatography.

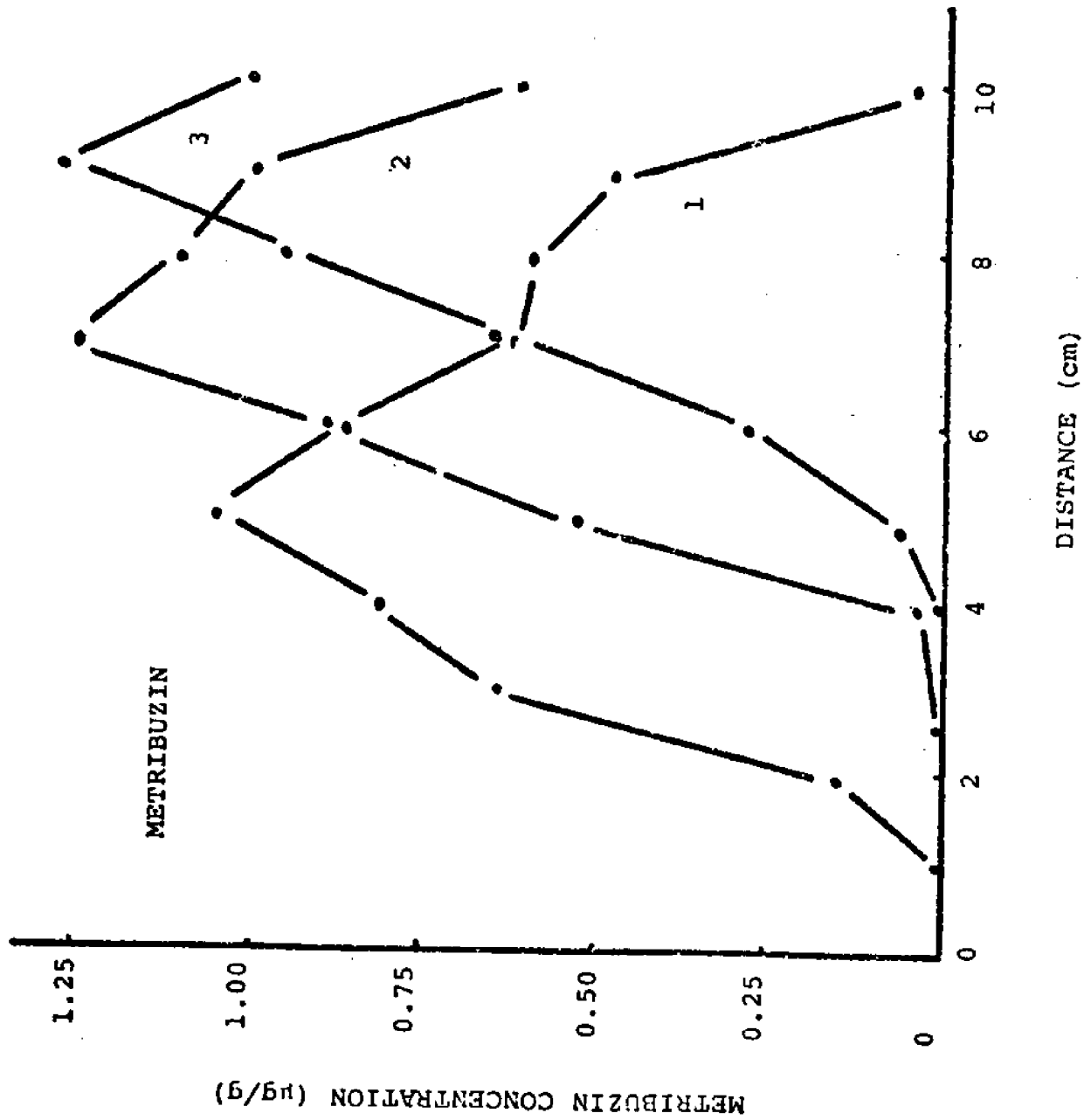


Figure 4. Mobility of metribuzin on soil thin layer plates with repeated elutions.

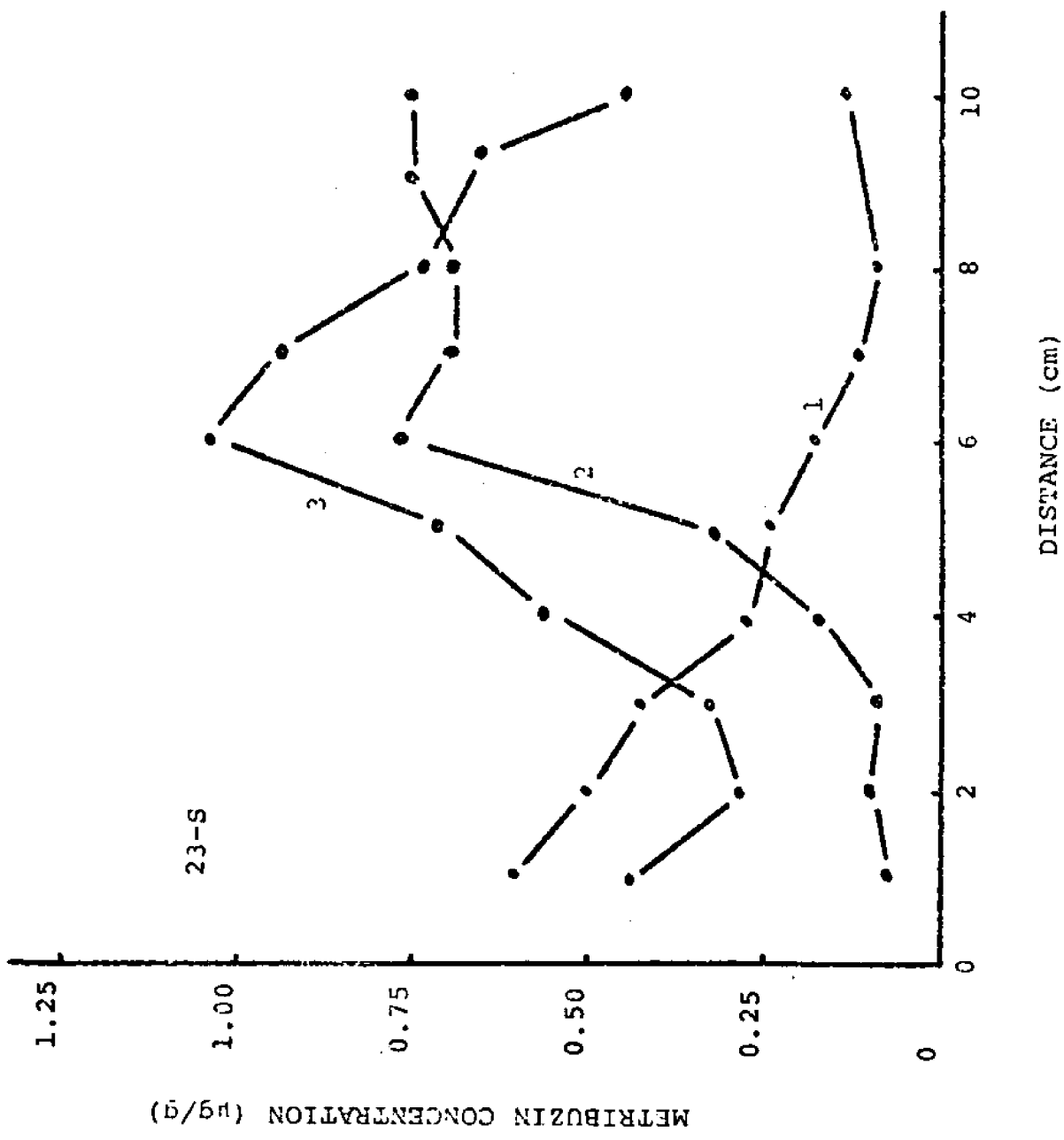


Figure 5. Mobility of metribuzin released from 23-S on soil plates with repeated elutions.

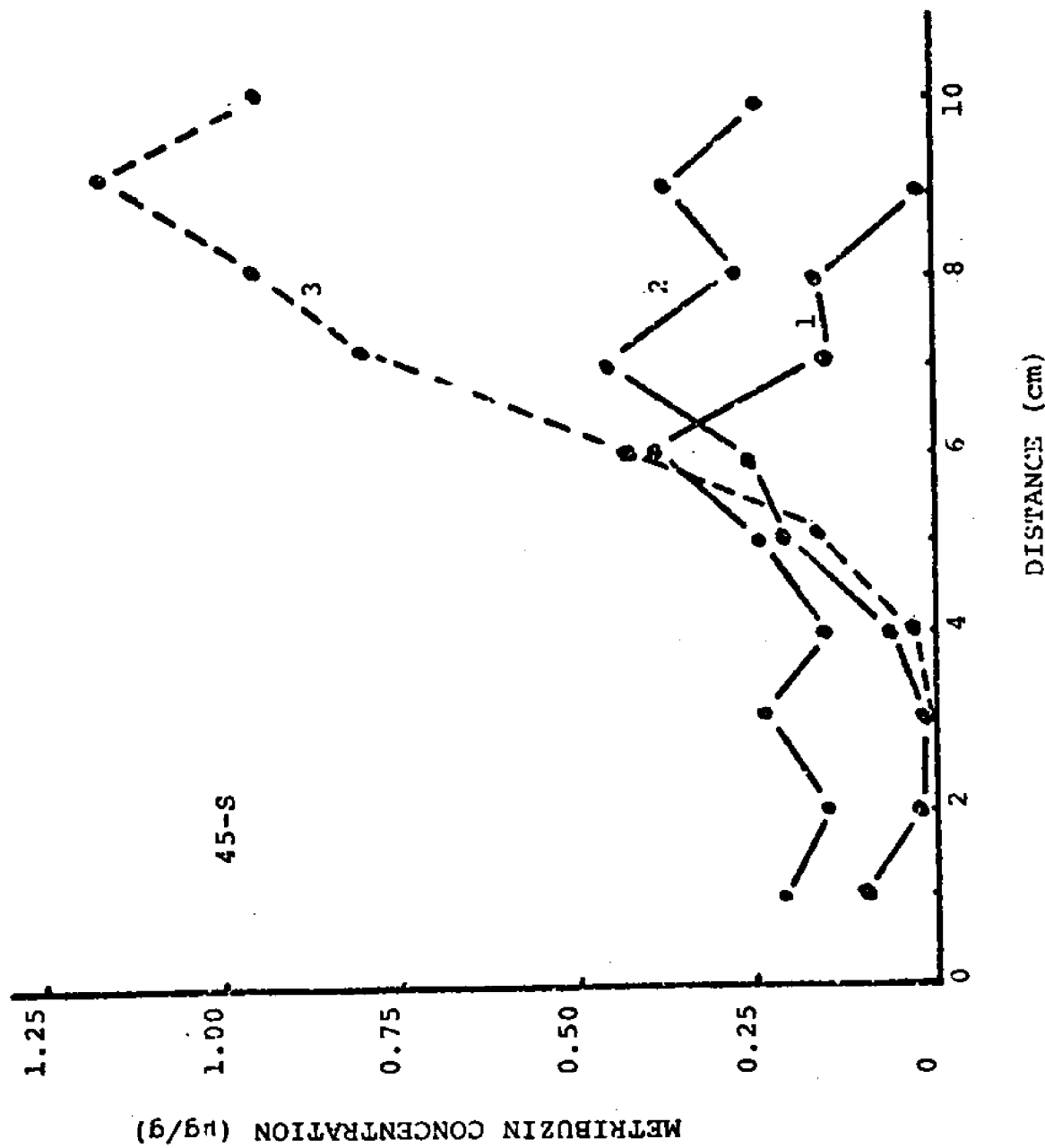


Figure 6. Mobility of metribuzin released from 45-S on soil plates with repeated elutions.

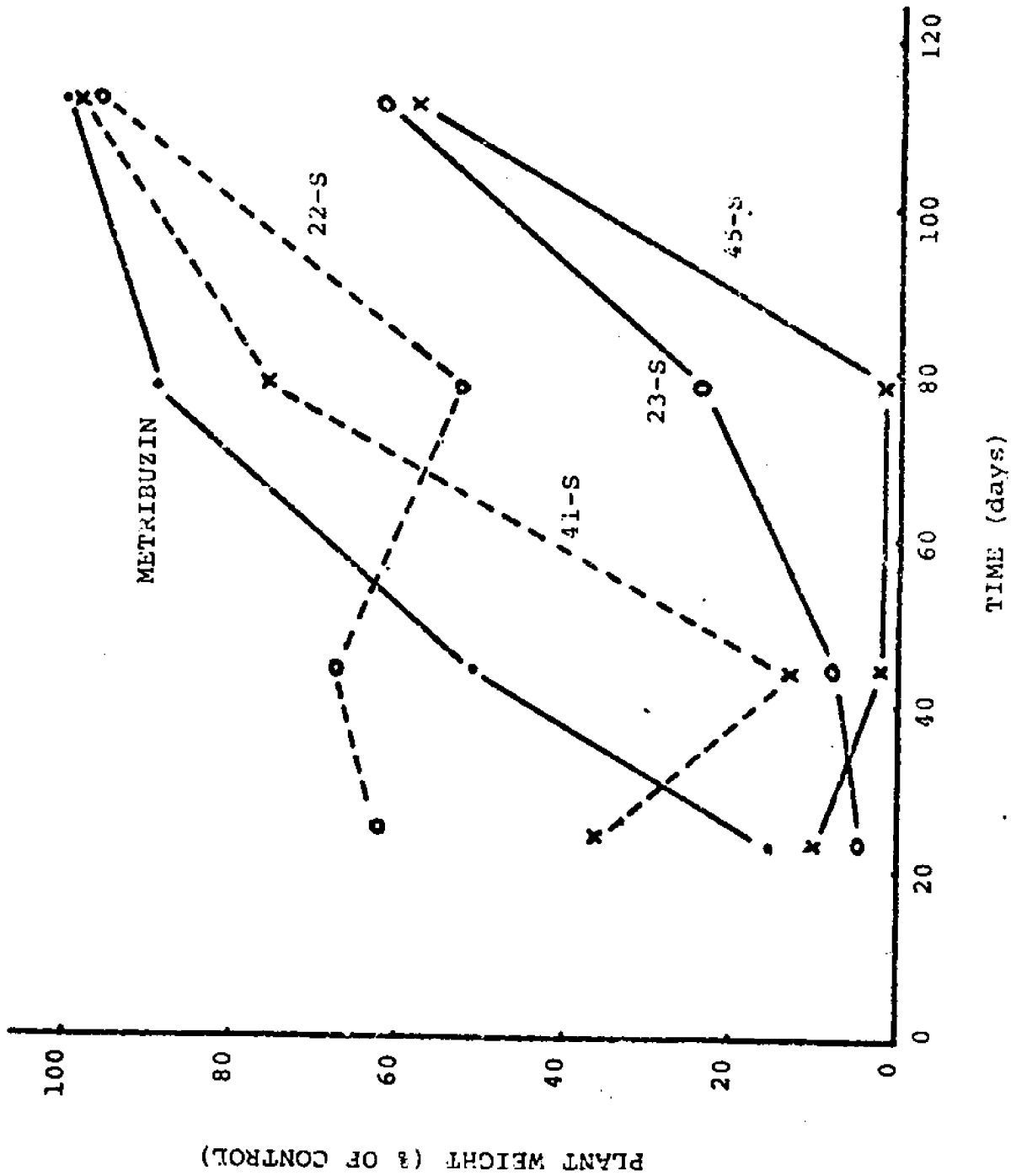


Figure 7. Residual phytotoxicity of metribuzin and four polymer systems containing pendant metribuzin to a mixture of seed species.

