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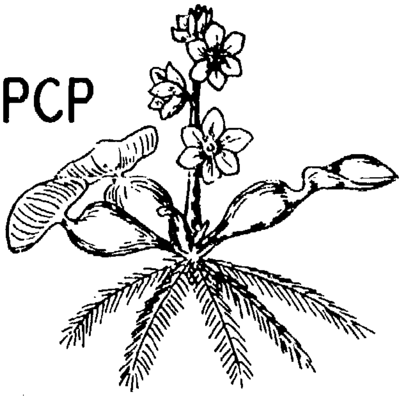

AQUATIC PLANT CONTROL PROGRAM

Technical Report 1

CONTROLLED-RELEASE HERBICIDES

SPONSORED BY: Office, Chief of Engineers
U. S. Army

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Waterways Experiment Station
Vicksburg, Mississippi

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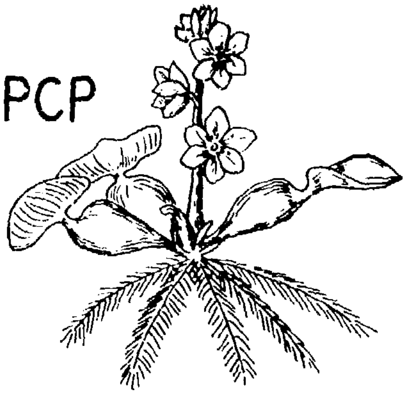

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FOREWORD

The current focus of attention on the natural environment has pointed up the fact that more information is available on the effects of herbicides on the environment than of most other chemicals. This is primarily due to the environmental considerations that were necessary for the research and development of these chemicals and, coincidently, that most herbicides are applied in water solution and are biodegradable.

Available data show that most crop plants that are treated with herbicides absorb only a small amount of chemical, and that most of these residues are rapidly eliminated from the animal body by the excretory system. Moreover, the animal body is able to metabolize and/or detoxify these chemicals at the levels of residue that are ingested under recommended treatment applications.

Research studies (1968 through 1972) that are summarized in this report were initiated to (a) minimize the amount of herbicide necessary for efficacious control, (b) maximize the treatment application for a specific target species, and (c) modify the system application for more complete control of the target species. Even though these goals have not been fully achieved, substantial progress has been made. It seems reasonable to anticipate that these goals will be met in the near future.

During the past decade, it has been a popular political assault to condemn herbicide manufacturers, agricultural and industrial users, and the research scientists who have developed these chemicals, but there is no real evidence to support this position. Indeed, the public interest has been well protected by dedicated and honest men who have

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sought to accomplish these difficult goals through long and tedious efforts, motivated by a deep sense of public service.

The Corps of Engineers involvement in this research effort stems from the adverse effects these obnoxious aquatic plants have on navigation as outlined in the legislation of the River and Harbor Acts, first approved by the Congress in 1899. Authority for the present program is delineated in section 302 of the 1965 act, for control of aquatic plants in the interest of navigation, flood control, drainage, and recreation.

Edward O. Gangstad, FAIC

CONTENTS

CONTROLLED-RELEASE HERBICIDES*

by

Edward O. Gangstad, Ralph H. Scott, Jr., and Raymond G. Cason**

PART I: INTRODUCTION

Aquatic Weed Control

1. Since the beginning of irrigated agriculture, man has struggled with aquatic weeds to control them by hand-clearing methods. During the past decade research efforts have been focused primarily on herbicides, and many thousands of new chemicals have been evaluated. From this evaluation, only a few have been successfully applied. The present responsibility of the aquatic weed scientist is to research herbicide application methods that will cause as little harm to the environment as possible. The problem is made extremely complex by many interrelated ecological factors. The program reported herein is an attempt to bring together a number of related phases of the study for a more adequate evaluation of the total problem.

Level of Application

2. One means of accomplishing this objective is to devise application techniques that result in low levels of herbicides in water, and

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* Contribution of the Planning Division, Directorate of Civil Works, Office, Chief of Engineers, Washington D. C. Preliminary report presented to the Weed Science Society of America Meeting, New Orleans, La., 13-15 Feb 1968.

** Chief, Aquatic Plant Control Program, DAEN-CWP-V, Washington D. C.; Plant Physiologist, Department of Defense Safety Board, formerly with the Corps of Engineers; and Agronomist, U. S. Agency for International Development, Lima, Peru, formerly with the Corps of Engineers, respectively.

retain low concentrations for periods long enough to kill undesirable aquatic vegetation. Results from preliminary studies show that suitable carrier systems can be developed that will control the release of herbicides in an aquatic environment. The seriousness of the present aquatic weed problem makes it imperative that all possible means be explored to solve the problem. For this reason, the U. S. Army Corps of Engineers supported a proposal by the U. S. Department of Agriculture, Field Plantation Laboratory, Fort Lauderdale, Fla., on the study of carrier systems involving polyvinyl chloride, rubber elastomers, clay, and other materials that might become available. Other contracts were made with the U. S. Army Environmental Hygiene Agency, Edgewood Arsenal, for the formulation of plastomer carriers and with the University of Akron for elastomer carriers. Critical levels of herbicide in the water after treatment as related to concentrations normally used in the control of water hyacinth and other aquatic plants were studied at the University of Southwestern Louisiana, both in the laboratory and in the field.

PART II: PROGRAM DEVELOPMENT

Technique of Application

3. The earliest report on the use of herbicides on carriers was by Oborn et al., 1954, who used 2,4-D pellets for the control of Potamogeton. Since that time, the use of granular formulations of herbicides has become quite common. The primary purpose in applying herbicides in granular form is for selective placement. The main types of granules are sinking granules that release the herbicide near the bottom for the control of submersed plants and floating granules that release the herbicide at the water surface for control of floating and emergent vegetation. The concept of releasing chemicals slowly over long periods of time is fairly new. This technique was first used to control mosquitoes, barnacles, and snails.

Fort Lauderdale Program

4. Research by the U. S. Department of Agriculture at Fort Lauderdale on the use of herbicide carrier materials for control of aquatic weeds has been in progress since 1964. A number of sinking and floating granules incorporating various herbicides for control of alligator weed and water hyacinth have been evaluated. In other studies, observations were made of the control of the submersed plant Hydrilla verticillata by mechanical mowing of dense growths of the plant and then application of weighted formulations of herbicides near the bottom. This method also reduced the amount of chemical needed for control.

5. A 2-yr cooperative study with the Corps of Engineers was initiated in July 1968 to assess the technique of zonal applications of herbicides. The first year of the study involved investigations of the effects of herbicides applied to isolated regions of intact plants. The results of these investigations showed that translocation of herbicides

did not occur in the submersed plants studied, and that control of these plants required total contact of plant and chemical. Control of floating water hyacinth, however, can be obtained through herbicide treatments to either root or shoot zones.

6. Research on the use of slow-release materials for control of aquatic plants has been in progress for approximately 2 yr. Polyvinyl chloride, rubber, and clay pellets containing herbicides, as well as encapsulation of herbicides, are some of the formulations presently being evaluated in this program.

7. Some preliminary results indicate that there is a definite advantage in the use of slowly released herbicides. A slow-release clay pellet of the amine salts of endothall showed promise for control of hydrilla. A clay pellet of endothall plus copper sulfate is currently being evaluated. Encapsulations of Diquat, endothall, copper sulfate, and other herbicides were evaluated in the laboratory and outside growth pools, and now are being evaluated in the field.

8. Preliminary results from static water bioassays indicate that herbicides are released from polyvinyl chloride carriers at rates sufficient to build up toxic concentrations in the plant tissues. Unless these materials are to be used only under static water conditions, the critical tests will be in flowing water situations. Relations between herbicide concentrations in water and contact time with the plant tissue will need to be determined in order to design carriers with the proper release rates. These data will be required for each plant-herbicide combination. With a better understanding of the relation between concentration and contact time, it should be possible to increase the probability of achieving satisfactory weed control under various conditions of water movement.

Research Objective

9. Conventional methods for controlling submersed aquatic plants

with herbicides include total volume treatments. The phytotoxic or lethal concentrations of herbicides must be reached in the entire volume of water to obtain effective aquatic weed control. The damage to nontarget organisms--both plant and animal--within a body of water, can be quite severe, depending on the toxicity of the herbicide. Applying herbicides in various inert carriers to give slow release over a long period of time is appealing for many reasons. Rather than having to treat the entire volume of water, it is possible, with selected carriers, to release the herbicide near the bottom where the plant growth originates and where the propagating plant organs are located. By proper timing of application, it should be possible to prevent the dense growths of aquatic plants by inhibiting or preventing growth early in the spring. The proper release rate of herbicides from the carriers theoretically should control any further new growth that might emerge from propagating structures buried in the bottom mud, a location which renders them immune from conventional treatments.

10. By proper design of release rates, it may be possible to adjust the release of the herbicides to the rate of absorption of the herbicide by the plants. The amount of chemical in the water at any time would be minimal and would reduce the amount of chemical pollution in the environment.

11. It would be economically advantageous to treat only a portion of the volume of water in which aquatic weeds are growing, rather than the whole volume of water. Additional operational costs would be reduced if fewer treatments were required to control aquatic plants.

Slow-Release Carrier Systems

12. The effectiveness of slow-release formulations should be evaluated in the laboratory, growth pool, and field. The advantages that justify this treatment, as listed above, can result in better control. Objectives of the research are to:

a. Determine the relation between herbicide concentration and phytotoxicity for different exposure times using conventional formulations of herbicides. Utilizing the the information from these experiments, design slow-release formulations. Evaluate these formulations for herbicidal effectiveness under various rates of water flow.

b. Compare the various slow-release formulations in growth pool experiments for effectiveness on eurasian water milfoil (*Myriophyllum spicatum*), hydrilla (*Hydrilla verticillata*), and southern naiad (*Najas guadalupensis*).

c. Determine the stage of plant growth when slow-release formulations would be most effective.

d. Evaluate the most promising formulations in small field plots, lakes, and canals.

e. Determine the toxicity of the various formulations to three species of fishes.

PART III: RESEARCH STUDIES

Agricultural Research Center Studies

13. Results of laboratory and growth pool evaluations of controlled-release herbicide formulations indicate that low-level release of 2,4-D butoxyethanol ester (BEE) was effective on water milfoil but not on hydrilla or naiad (see figs. 1 and 2). Of the herbicides studied only the Fenac formulation could be expected to maintain a phytotoxic level for a sufficient period of time to prevent regrowth of water milfoil. Controlled-release formulations were not toxic to fish. Details of the study are presented in Appendix A.

Edgewood Arsenal Studies

14. Results of laboratory evaluations indicate that polyvinyl chloride (PVC), biodegradable rubber, and encapsulated formulations are capable of controlled release. The PVC carrier system is not particularly suitable for field application. Several 2,4-D BEE biodegradable rubber formulations were found satisfactory, and should be considered for further testing. Preliminary evaluation of encapsulated formulations of the alkanolamine salts of 2,4-D indicate that the products should also be further studied. Detailed information of this study is presented in Appendix B.

University of Akron Studies

15. Results of the research program of development of herbicidal formulations by the Creative Biology Laboratory at the University of Akron indicate that biodegradable rubber does offer a potential carrier system for the development of slow-release herbicides. To facilitate such a mechanism, it was necessary to study chronic toxicities of the target species, in order to simulate conditions that would obtain in the field where such a mechanism was to be used. Additional studies are needed to correlate these effects with field trials. Preliminary results

of the product development research are presented in Appendix C.

University of Southwestern Louisiana Studies

16. Dissipation of 2,4-D residues in ponds, lakes, bayous, and other quiescent or slowly moving bodies of water following treatment to control aquatic vegetation is summarized in Appendix D. For the standard treatment, i. e. 4 lb acid equivalent per acre, the dissipation rates are: 58 parts per billion (ppb) decrease in residue for each 2-ft depth of water treated, 115 ppb decrease in residue for each 10 F increase in temperature above 60 F mean temperature, and 53 ppb decrease in residue for each 7-day interval of time after treatment.

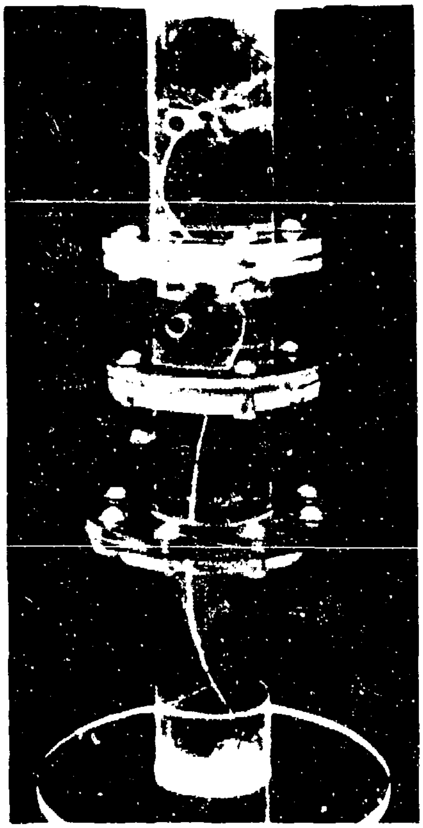
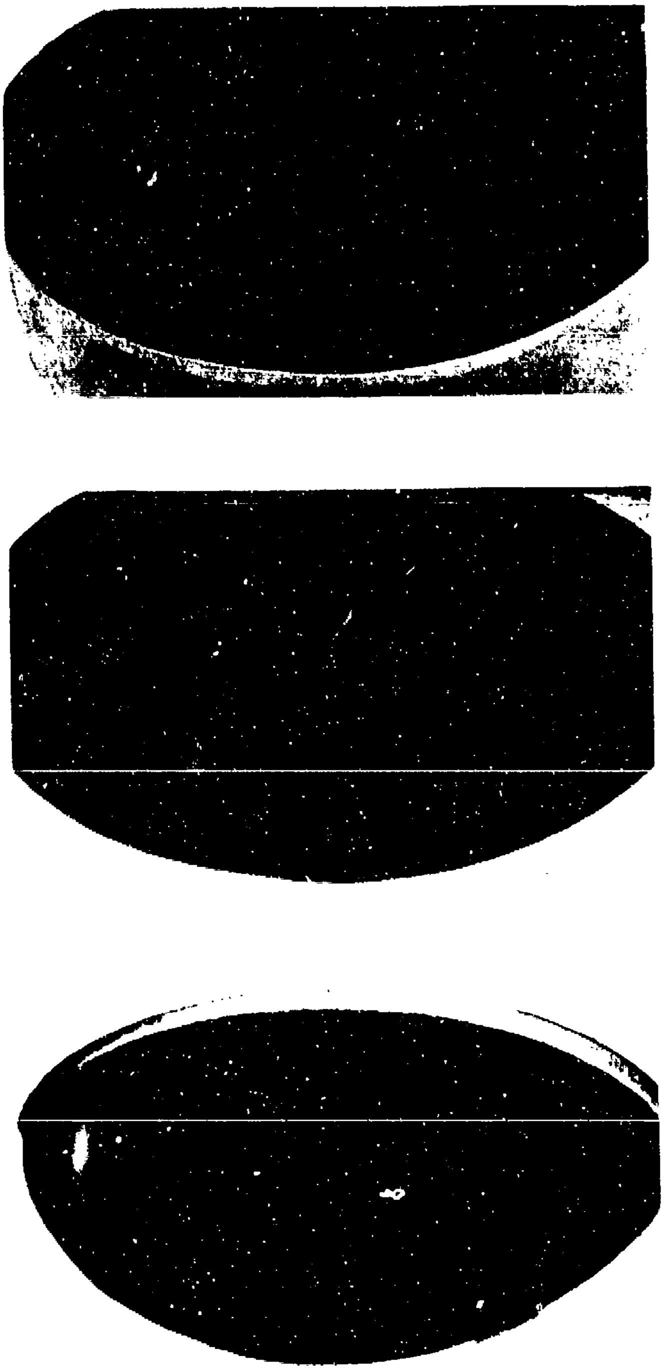


Fig. 1. Plexiglas apparatus for phytozone treatments to milfoil plants growing in a vertical position. Gaskets and eicosane isolate plant regions at the flanges. Translocation of herbicides in milfoil is minimal, and effective treatments must include regrowth of fragments by a sustained or recurring application



Pretreatment control

10 days post-treatment effect

10 weeks post-treatment effect

Fig. 2. 2,4-D BEE treatments at 2 ppm with attaclay granules in outdoor pools

APPENDIX A

EVALUATION OF CONTROLLED-RELEASE HERBICIDAL FORMULATIONS FOR AQUATIC WEED CONTROL

U. S. Department of Agriculture
Agricultural Research Center
Fort Lauderdale, Fla.

EVALUATION OF CONTROLLED-RELEASE HERBICIDAL FORMULATIONS FOR AQUATIC WEED CONTROL*

by

Kerry K. Steward**

Abstract

Laboratory Bioassays. Four of six controlled-release rubber formulations of 2,4-D evaluated on submersed weeds were effective on water milfoil. One was effective at 1.0 ppmw concentrations. None were effective on hydrilla or naiad. A sinking granule containing Diquat was effective on all three submersed weeds, but less effective on hydrilla than the conventional liquid treatment.

Growth Pool Bioassays. All six controlled-release formulations evaluated in outdoor growth pools produced complete control of water milfoil plants by the fifth week after treatment. The results indicated that only Fenac could be expected to maintain phytotoxic herbicide levels in water sufficient to control regrowth of water milfoil.

Herbicide Contact Time Versus Concentration Study. Injury to water milfoil plants increased with both increasing herbicide concentration and exposure time. It was determined that 1.0-ppmw concentrations of 2,4-D BEE in contact with the plants for 48 hr were required for complete kill of the test plants.

Toxicity of Controlled Release Formulations to Fish. None of the formulations appeared to be toxic to test fish. At no point in the evaluations did the mortality of the treated fish appear significantly higher than that in the control fish.

Introduction

1. Applying herbicides in various inert carriers for aquatic weed

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* Research contribution, U. S. Department of Agriculture, Agricultural Research Center, Fort Lauderdale, Fla.

** Plant physiologist and principal investigator, Plant Sciences Division.

control is appealing for a number of reasons. Rather than treating the entire volume of water, it may be possible, with selected carriers, to release the herbicide near the bottom where the plant growth originates and where the propagating structures are located. Proper timing of application may prevent dense growth of aquatic plants by inhibiting or preventing growth early in the growing season. Controlled release of herbicides from the carrier may control any further new growth that might emerge from propagating structures buried in the bottom mud, a location that renders them immune from conventional treatments.

2. It may be possible to adjust the release of the herbicides to the rate of absorption by the plants. The amount of chemical in the water at any time would be minimal and would reduce the amount of chemical residue in the aquatic environment.

3. It would be more economical to treat only the volume of water in which the weeds are growing rather than the entire volume of a body of water. Controlled-release herbicides may add savings in operational cost if fewer treatments or applications are required.

4. A cooperative program to evaluate the efficacy of controlled-release herbicide formulations has been in progress since early 1970. The results of investigations conducted during this period indicated that polyvinyl chloride (PVC) and rubber formulations of (2,4-dichlorophenoxy) acetic acid (2,4-D) and PVC formulations of (2,3,6-trichlorophenyl) acetic acid (Fenac) were sufficiently promising to warrant further study. The results of these and other studies relating to the concept of aquatic weed control with controlled-release herbicide formulations is the subject of this report.

5. The study was designed to meet the following objectives:

   a. To evaluate in the laboratory the phytotoxicity to aquatic weeds of experimental controlled-release herbicide formulations supplied by cooperators.

   b. To compare promising formulations in outdoor growth pool experiments by determining the ability of the various formulations to maintain phytotoxic herbicide concentrations in water during these experiments.

c. To determine the toxicity of the controlled-release formulations to different species of fish.

d. To determine the relation between herbicide concentration and phytotoxicity for different exposure times using conventional formulations of herbicides. The information from these experiments may be utilized to design formulations with appropriate herbicide release rates.

Laboratory Bioassays

Methods and materials

6. The basal portions of apical cuttings (4-6 in.) of the submersed plants southern naiad (*Najas guadalupensis* (Spreng.) Magnus), hydrilla (*Hydrilla verticillata* Casp.), and eurasian water milfoil (*Myriophyllum spicatum* L.) were placed in 2-in. square pots filled with a sandy loam soil. The potted plants were placed in 1-gal wide-mouthed glass jars that had been previously filled with 3500 ml of pond water and fertilized with 5 drops of a 12-6-6 fertilizer. The culture jars were covered with clear plastic wrap to retard evaporation and prevent contamination from airborne spores. The jars were then placed in a temperature- and light-controlled room. The temperature was maintained at approximately 25 C. Light intensity was approximately 200 footcandles (ft-c) with a 12-hr photoperiod. In approximately 3 weeks, the plants were rooted and well established in the jars and were ready to be used in the evaluation tests. Water hyacinth plants (*Eichhornia crassipes* (Mart.) Solms) were collected from local canals and established in the greenhouse in 3-gal plastic containers lined with 2-mil polyethylene bags. Three weeks after being established, plants were treated with the experimental formulations and placed in another greenhouse for observation of herbicidal effects.

7. The treatment rates used in the evaluations were based on the weight of active ingredient in the various formulations. For example, a 1.0-ppmw rate requires 3.5-mg of active ingredient for 3500 ml of water. It was necessary to subdivide individual pellets of the

experimental formulations to obtain the small quantities required for low concentrations. Each treatment rate was replicated a minimum of three times. The herbicidal effects were recorded at periodic intervals following treatment. A rating scale of 0 to 100 was used, with 0 being no effect and 100 being a complete kill.

8. Experimental formulations were supplied by cooperating agencies. Polyvinyl chloride (PVC) formulations and 6,7-dihydrodipyrido=(1,2-a:2',1'-c) pyrazinediium ion (Diquat) granules were supplied by the U. S. Army Environmental Hygiene Agency (USAEHA), Edgewood Arsenal, Md. The rubber formulations were supplied by the University of Akron, Product Development Laboratory, Akron, Ohio. Commercial formulations were supplied by individual chemical manufacturing companies (see table A1).

Results and discussion

9. The effects on various submersed weeds of 2,4-D formulated in rubber are shown in table A2.

10. The compounds coded 11ACE-Cl, 11ACE-E, 14ACE-B, and 18ACE-B were effective on the phenoxy-herbicide-susceptible water milfoil. The compound 14ACE-B was the only formulation that was effective at 1-ppmw concentrations and can be considered the most effective. Southern naiad and hydrilla are not normally affected by phenoxy herbicides, except at very high treatment rates. The 11ACE-E and 18ACE-B formulations were slightly phytotoxic to naiad. None of the formulations affected hydrilla.

11. The results of evaluations with Diquat granules on submersed weeds are given in table A3. The granules were effective on both naiad and water milfoil. However, the granules were less effective on hydrilla than the standard treatment. In general, hydrilla is the most herbicide resistant of the three plants that were tested. Hydrilla is normally controlled in the laboratory and in the field with the standard Diquat formulation at a rate of 0.5 ppmw. The lack of control with the granules at the 1-ppmw rate is indicative of inadequate

Table A1

Composition of Controlled-Release Herbicide Formulations

Formulations	Compositions
PVC	
2,4-D acid	30%, by weight, of (2,4-dichlorophenoxy) acetic acid
Base 89A*	30%, by weight, of the technical grade butoxyethanol ester of 2,4-D (69.3% acid equivalent)
LV-4*	30%, by weight, of the commercial grade butoxyethanol ester of 2,4-D (43% acid equivalent). This commercial formulation contains aromatic oil, diluents, and emulsifying agents. The product is oil soluble and emulsifiable in water.
Fenac	30%, by weight, of technical grade (2,3,6-trichlorophenyl) acetic acid (70% acid equivalent)
Rubber	All rubber compounds were formulated with technical grade butoxyethanol ester of 2,4-D (Base 89A, 69.3% a.e.)
10ACE-E	15.8% Base 89A
11ACE-C1	12.5% Base 89A
11ACE-E	29.0% Base 89A
14ACE-A	22.2% Base 89A
14ACE-B	22.2% Base 89A
15ACE-B	37.5% Base 89A
15ACE-B-(L)	37.5% Base 89A
18ACE-B	33.5% Base 89A
Bouquet	20.0% Base 89A
Other	
Diquat**	10%, by weight, of technical Diquat (100% a.i.) on a mineral base 8/15 mesh granule
Capsules†	23% acid equivalent, by weight, of alkanol amine salt (ethanol and isopropyl series) of 2,4-D

* Product of Amchem Products, Inc., Ambler, Penn.

** Product of GAF Corporation, Research Mineral Products, Hagerstown, Md.

† Product of Minnesota Mining and Manufacturing Co., St. Paul, Minn.

Table A2

Evaluation of the Herbicidal Activity of 2,4-D Formulated in Rubber Pellets

Formulation	Treatment Rate ppmw	Avg % Control, Weeks After Treatment (3 Replicates) — Naiad 2	Naiad 4	Naiad 6	Hydrilla 2	Hydrilla 4	Hydrilla 6	Water Milfoil 2	Water Milfoil 4	Water Milfoil 6
10ACE-E	1	0	0	0	0	0	0	0	0	0
	5	0	0	0	0	0	0	0	0	0
	10	2	2	8	0	0	0	0	2	7
11ACE-Cl	1	2	2	0	0	0	0	0	5	3
	5	0	0	0	0	0	0	32	63	87
	10	0	0	0	0	0	0	50	95	99
11ACE-E	1	0	0	0	0	0	0	5	18	18
	5	23	37	30	5	8	3	82	85	88
	10	7	28	42	5	2	8	43	93	96
14ACE-B	1	0	0	0	0	0	0	37	83	100
	5	0	0	0	0	0	0	43	100	100
	10	0	0	0	0	0	0	53	100	100
15ACE-B	1	5	0	3	0	0	2	0	3	7
	5	3	3	7	0	2	2	3	5	17
	10	0	2	0	2	0	0	2	10	8
18ACE-B	1	0	0	0	0	0	0	0	20	30
	5	20	22	27	10	7	7	30	43	44
	10	13	10	20	0	0	5	47	79	84
Control		0	0	0	0	0	0	0	0	0

Table A3

Static Water Evaluation of Diquat Formulated in Controlled-Release Sinking Granules (10% a.i.)

Formulation	Treatment Rate ppmw	Avg % Control, Weeks After Treatment (3 Replicates)											
		Naiad				Hydrilla				Water Milfoil			
		2	4	6	8	2	4	6	8	2	4	6	8
Granule evaluation 1	1	97	100	100	100	13	40	65	67	77	99	100	100
	5	91	100	100	100	35	82	95	95	96	99	100	100
	10	94	100	100	100	25	93	100	100	28	100	100	100
Granule evaluation 2	1	98	100	100	--	7	38	70	--	90	100	100	--
	5	98	100	100	--	10	89	100	--	88	100	100	--
	10	98	100	100	--	15	100	100	--	88	100	100	--
Liquid standard	0.5	52	100	100	100	35	98	100	100	10	98	100	100

herbicide release from the granules.

12. The results of evaluations of the Diquat granules on water hyacinth are given in table A4. In these tests the granules were compared with the standard formulation applied to the foliage or injected below the water surface. These results indicated that the granules were not as effective as the standard foliar application. The comparison with the water-injection treatment indicated that the 0.5-lb/A (pound per acre) rate of the water-injection treatment gave satisfactory control 6 weeks after treatment. In order to obtain comparable results with the granules, a 2-lb/A rate was required. Applying Diquat on a granule to control water hyacinth would require that the granule be a floating type since Diquat would be inactivated by bottom sediments if applied as a sinking granule. The results of evaluations with this granule indicated that Diquat was released from the granule at a rate sufficient to produce phytotoxic concentrations in water. The formulation appeared sufficiently promising to recommend further evaluations.

13. The results of evaluations on water hyacinth with 2,4-D and Fenac formulated in PVC and rubber are given in table A5. The compound coded 18ACE-B was the most effective of the rubber formulations tested. The next most effective formulation was the compound coded 14ACE-A.

Table A4

Evaluations of Diquat Liquid Versus Granular Formulations on Water Hyacinth

Method of Application	Treatment Rate lb/A	Avg % Control, Weeks After Treatment (3 Replicates)			
		1	2	4	6
Foliar spray (liquid)	2.0	90	100	100	100
	1.0	85	98	100	100
	0.5	80	95	100	100
	0.25	70	88	100	100
	0.125	68	88	100	100
Water injection (liquid)	2.0	50	80	100	100
	1.0	45	80	100	100
	0.5	20	50	96	100
	0.25	5	20	43	89
	0.125	0	0	7	37
Granular	2.0	20	50	85	99
	1.0	5	18	25	83
	0.5	0	8	10	35
	0.25	0	2	4	7
	0.125	0	0	0	0.7
Control		0	0	0	0

Table A5

Evaluations of the Herbicidal Activity of Slow-Release Formulations of 2,4-D and Fenac on Water Hyacinth

Formulation	Treatment Rate lb/A	Percent Control, Weeks After Treatment					
		1	2	4	6	8	10
		Rubber					
11ACE-E	5	0	0	0	0	0	--
	10	0	0	0	0	0	--
14ACE-A	5	0	0	5	3	3	0
	10	1	7	40	47	60	68
14ACE-B	5	0	0	0	0	0	--
	10	0	0	0	5	3	--
15ACE-B	5	0	0	0	0	0	0
	10	0	5	10	10	10	8
15ACE-B-(L)	5	0	0	0	0	0	0
	10	0	0	0	0	0	0
18ACE-B	5	0	0	0	0	0	0
	10	3	10	65	97	100	100
Bouquet (20% a.i.)	5	0	0	0	0	0	0
	10	0	2	13	38	40	38
		PVC					
30% Fenac	5	5	10	20	40	60	--
	10	10	17	37	60	80	--
30% 2,4-D LV-4	5	0	0	0	0	0	--
	10	0	0	0	0	0	--
30% 2,4-D Base 89A	5	0	0	0	0	0	--
	10	0	0	0	0	0	--
		Liquid Standards					
Fenac	1	50	63	97	98	100	--
	2	60	75	100	100	100	--
2,4-D	2	15	25	90	98	100	100
	4	25	50	98	100	100	100
Control	0	0	0	0	0	0	0

Not one of the remaining rubber formulations was effective. Fenac was the only effective herbicide within the PVC formulations. Neither of the 2,4-D formulations in PVC was effective.

14. Wilkinson* investigated the release of several derivatives of phenoxy herbicides into water from clay granules. He observed that the rate and quantity released were greater for the acid than for the butoxyethanol ester (BEE). Increased water solubility was found to be associated with increased rate and quantity of desorption from the granules. The solubility in water of 2,4-D acid is 600 to 700 ppmw (at 20-30 C). The BEE of 2,4-D is essentially insoluble in water.**

15. The acid and BEE derivative of 2,4-D on water milfoil were evaluated to determine if differences in phytotoxicity could be obtained. Comparisons were made between the acid and BEE formulated in PVC and the unformulated compounds that were prepared in acetone and applied to water in jars. The granules were formulated of PVC at 30% (a.i.) concentrations.

16. The results of evaluations of the acid and the BEE derivatives of 2,4-D on water milfoil are given in table A6. When formulated in PVC, the acid was more effective than the ester. There was essentially no difference between the controls and the jars treated with the ester in PVC.

17. When applied in solution, the ester was more effective on water milfoil than was the acid. The ester produced a phytotoxic response earlier and at a lower concentration than did the acid. The injury to the plants in the 0.25-ppmw acid treatments was probably due to the acetone since injury in the acetone checks increased in a similar manner.

18. When formulating 2,4-D in plastomers, there may be an

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* R. E. Wilkinson, "Subaqueous Release of Herbicides from Granules," Weeds, Vol 12, 1964, pp 69-76.

** Herbicide Handbook of the Weed Science Society of America, 2d ed., Humphrey Press, New York, 1970.

Table A6

Effects on Water Milfoil of 2,4-D Acid and the BEE Derivative of 2,4-D Applied in Solution and in PVC Formulations

Herbicide and Formulation	Treatment Rate ppmw	Percent Control, Weeks After Treatment 1	2	4	6	8	10
Acid in PVC	0.25	3	7	5	7	12	38
	0.50	7	13	15	15	15	42
	1.00	23	30	33	38	40	65
Ester in PVC	0.25	5	7	5	5	5	7
	0.50	5	5	5	5	5	13
	1.00	5	12	13	20	10	12
Acid in solution	0.25	0	2	10	10	10	35
	0.50	0	2	47	50	68	93
	1.00	0	5	89	100	100	100
Ester in solution	0.25	0	38	93	98	100	100
	0.50	3	67	75	100	100	100
	1.00	0	73	97	100	100	100
Acetone check (2 ml per gal)	--	2	0	0	10	17	23
Controls	--	0	3	3	3	3	6

advantage in utilizing 2,4-D acid rather than the ester, since release into water appears to be greater for the acid than for the ester.

Growth Pool Bioassays

Methods and materials

19. Water milfoil plants were collected in August 1970 at Crystal River, Fla., and transplanted into 1000-gal plastic-lined growth pools at the Fort Lauderdale Field Station. The basal ends of 9- to 12- in. cuttings were anchored in 6 in. of a 1:1 mixture of sand and peat soil

in the pools. Individual plants were spaced approximately 3 in. apart. The water level was raised gradually over a 2-week period to allow the plants to become rooted. Herbicide treatments were applied 15 Oct 1970, approximately 7 weeks after the pools were planted. Treatments were applied at 2.5- and 5.0-ppmw or 10- and 20-ppmw rates and were replicated three times. Water samples were taken from all 39 pools in the experiment for analysis of 2,4-D content. These data were to provide information on release rates of the herbicide from the formulations, persistence of the herbicide in water, and the relation between herbicide concentration in water and phytotoxicity to water milfoil.

20. The sampling and extraction procedures were as follows: A 1-qt sample was taken from each pool at middepth from three equal intervals around the circumference of the pool. A 250-ml aliquot was taken from each quart sample of each treatment replicate and composited.

21. A 500-ml aliquot of the treatment composite was then taken for extraction. The pH of samples from BEE treatments was adjusted to pH 12 with sodium hydroxide, mixed, and allowed to stand for 30 min. All samples were then acidified to pH 1-1.5 with concentrated hydrochloric acid and then extracted twice with 25-ml volumes of chloroform. The chloroform extracts were sent to CPT Larry Nelson, Edgewood Arsenal, Md., for analysis.

Results and discussion

22. All treatments in the pool bioassays produced an epinastic response in the plants after 24 hr. The degree of response increased with time. After 7 days, approximately half of the 39 pools in the experiment were experiencing a rapid growth of filamentous algal mats at the water surface. At this time, infestation and injury to the plants by the aquatic moth Parapoynx allionealis were also observed in approximately half of the pools. After 2 weeks, the herbicidal injury to the plants was more pronounced. The plants in the pools treated at the 20-ppmw rate had sunk to the bottom of the pools. The plants in the

10-ppmw treatments had dropped about halfway to the bottom. Both algal growth and insect damage had increased at this time. After 3 weeks, the plants in treated pools were exhibiting various stages of advanced injury and decomposition. Algal infestation continued to proliferate. Insect activity decreased due to the decreased supply of healthy plants.

23. The quantitative results of the evaluations are given in table A7. All formulations at each concentration that was evaluated produced adequate control of water milfoil by the fifth week. A portion of the plant injury was due to the adverse growth conditions mentioned earlier. This is indicated in table A7 by the progressively increasing injury rate for the control pools. However, injury to treated plants

Table A7

Effects of Various Formulations of 2,4-D on Eurasian Water Milfoil Growing in Outdoor Pools

Formulation	Treatment Rate ppmw	Percent Control, Weeks After Treatment 1	2	3	4	5
Base 89A (PVC)	20	4	53	88	99	100
	10	3	40	70	97	100
LV-4 (PVC)	5.0	4	35	73	97	99
	2.5	2	43	65	96	100
14ACE-B (rubber)	5.0	2	42	83	97	100
	2.5	2	38	68	96	100
11ACE-E (rubber)	5.0	2	35	83	96	100
	2.5	2	17	77	97	100
Fenac acid (PVC)	5.0	4	35	72	95	100
	2.5	2	22	72	99	100
Alkyl amine (encapsulated)	5.0	3	35	73	88	98
	2.5	1	23	70	96	99
Control		0	3	22	43	81

increased more rapidly than did injury to the control plants.

24. There was little apparent difference in phytotoxicity between the formulations or even between treatment rates. The degree of injury was uniform throughout the treatments at each observation period (weeks after treatment). The degree of injury also increased uniformly with time. This pattern of response is indicative of a rapid release of herbicide from the formulations and a rapid buildup to phytotoxic concentrations. The lowest treatment rate (2.5 ppm) was more than adequate to control water milfoil in these tests.

25. After the milfoil plants in the pools were destroyed by herbicides or damaged by adverse growth conditions, it was no longer possible to assay the various formulations for efficacy in maintaining phytotoxic herbicide levels in the pools. In an attempt to overcome this loss, four water milfoil plants established in pots were introduced into each pool and evaluated for injury at periodic intervals. The results of these evaluations are given in tables A8 and A9. Only the formulations of Fenac maintained effective phytotoxic concentrations in the pools (table A8). The potted plants placed in the Fenac-treated pools were killed in about the same amount of time (4 weeks) required for the original plants to be killed (table A7).

26. Because persistent residues in the Fenac-treated pools destroyed the introduced plants, it was necessary to continually replenish dead plants with new healthy plants in order to continue the bioassay. Plants were replaced when no living tissue was discernible. Since the plants were not replaced at any set interval, the results of these bioassays are expressed in table A9 as the average length of time required for 100% control of the plants.

27. The evaluations were carried out over periods ranging from 77 to 235 days after the initial treatments. Over this period of time, survival of introduced plants varied from 28 to 44 days. These results indicate that phytotoxic concentrations of Fenac were being maintained in the pools through 235 days after treatment. The tests were terminated at that time.

Table A8

Effects of Various Formulations of 2,4-D on Eurasian Water Milfoil Introduced into Pools 77 Days After Initial Pool Treatments

Formulation	Treatment Rate ppmw	Percent Control, Days After Treatment 81	88	95	108	122	136
Base 89A (PVC)	20.0	3	8	20	35	32	13
	10.0	5	17	47	53	53	47
LV-4 (PVC)	5.0	0	8	42	60	70	60
	2.5	0	7	8	33	43	18
14ACE-B (rubber)	5.0	5	13	18	13	8	10
	2.5	1	5	8	12	8	8
11ACE-E (rubber)	5.0	0	7	2	7	5	3
	2.5	1	6	10	8	0	0
Fenac acid (PVC)	5.0	7	13	62	98	100	100
	2.5	8	18	68	98	99	100
Alkyl amine (encapsulated)	5.0	2	5	50	41	47	47
	2.5	1	6	45	48	47	43
Control		0	0	2	8	5	2

Table A9

Days Required to Produce 100% Control of Water Milfoil Plants Introduced into Fenac-Treated Pools During Four Evaluation Periods

Treatment Rate, ppmw	Evaluation Period	Injury Evident, Days After Treatment	Evaluation Interval days*
5.0	1	37	77-123
	2	44	109-165
	3	36	165-207
	4	28	193-235
2.5	1	44	77-137
	2	28	123-165
	3	36	137-207
	4	28	165-235

Note: Injury to plants in control pools during entire evaluation period averaged 3%.

* Days after treatment during which evaluation period extended.

28. The results of water residue analyses to determine herbicide persistence are given in table A10. These data are tabulated in the order of decreasing persistence and release.

29. Fenac in PVC was the most persistent of all the formulations tested and was also the formulation that produced the highest residue level. The 5.0-ppmw treatments produced a 4.1-ppm concentration in the 56-day sample which was 82% of the amount applied initially.

30. The next highest concentration reached in the pools was in the treatments with the Base 89A (PVC) formulation. A concentration of 2.2 ppmw was measured in the 14-day sample and represents approximately 11% of the amount initially applied. The amount of active ingredient applied in this instance was four times greater than in the Fenac treatments, but resulted in lower residue levels.

31. The rubber formulation 11ACE-E produced maximum residues of

Table A1[illegible]

Residue Levels in Water of Ponds Treated with Controlled-Release Herbicide Formulations

Formulation	Treatment Rate ppm	[illegible]	1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]																						
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.41	[illegible]	[illegible]	[illegible]	1.9	1.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	1.[illegible]	[illegible]	1.[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.[illegible]	[illegible]	1.[illegible]	[illegible]	1.[illegible]	1.[illegible]	1.[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	1.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	--	--	--	--	--	--	--	--	--	--	--	--
	[illegible]	[illegible]	[illegible]	1.[illegible]	1.[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	--	--	--	--	--	--	--	--	--	--	--	--
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0	0	0	--	--	--	--	--	--	--	--	--	--	--	--
	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0	--	--	--	--	--	--	--	--	--	--	--	--
[illegible]	[illegible]	0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0	0	--	--	--	--	--	--	--	--	--	--	--
	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	--	--	--	--	--	--	--	--	--	--	--
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	--	--	--	--	--	--	--	--	--	--	--	--
	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0	--	--	--	--	--	--	--	--	--	--	--	--
[illegible]	[illegible]	0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0	[illegible]	[illegible]	0	0	--	--	--	--	--	--	--	--	--
	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0	--	--	--	--	--	--	--	--	--
Control		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

[illegible]

0.86 ppmw in the 14-day sample, which represents 17% of the possible treatment maximum. The rubber formulation 14ACE-B also produced a peak concentration at approximately 14 days. The PVC formulation of LV-4 was next, and the lowest residue levels were obtained from the encapsulated alkyl amine formulation. These levels were only 2% to 3% of the quantity originally applied.

32. Except for the Fenac acid, all residues had disappeared from water by the 98th day after treatment. The reason for the disappearance of the herbicides is not known at present, but could be due to absorption by plants and algae, through decomposition, or through precipitation.

33. The pattern of residue levels in water adds little to the overall picture. All treatment rates of all formulations were effective, even the encapsulated amine formulation which produced the lowest residue levels.

34. The results of tests completed in FY 70* revealed that herbicide levels in water treated at a 4-ppmw rate with Base 89A in PVC were not effectively maintained beyond 7 days. It was recommended that this compound be evaluated at higher treatment rates to determine if concentrations could be maintained for longer periods. A fivefold increase in treatment rate to 20 ppm resulted in maintaining a higher concentration in water over the same period. Residue levels were detectable for a shorter time in the present tests, however.

35. In the FY 70 tests, residues were detected through 42 days; whereas in the present test residues were below the level of detection after the same period. Except for Fenac, none of the formulations effectively maintained herbicide levels to 42 days. Residues of Fenac were still being detected nearly a year after treatment. The persistence of Fenac is primarily a function of the herbicide rather than the

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* Annual Report for FY 70. Cooperative Investigations Between the Corps of Engineers and USDA Aquatic Weeds Investigations.

formulations, since Fenac alone has been shown to resist microbial breakdown and to persist in aquatic habitats for 1 to 2 yr.*

36. The results of the bioassays and of the residue analyses indicate that of the six controlled-release formulations evaluated, only Fenac could be expected to maintain phytotoxic herbicide levels in water sufficient to control regrowth of water milfoil.

Herbicide Contact Time Versus Concentration Study

Methods and materials

37. The results of static water bioassays indicate that herbicides are released from controlled-release formulation at rates sufficient to produce phytotoxic concentrations. Unless these materials are to be used only under static water conditions, the critical tests will be in flowing water situations. The relations between herbicide concentrations in water and contact time with the plant must be determined in order to design carriers with the proper release rates. These data are required for each plant and herbicide combination. The purpose of these experiments was to obtain information of the relation between the concentrations of 2,4-D BEE in water and phytotoxicity to water milfoil following various periods of exposure to the various concentrations of herbicide.

38. Apical cuttings of water milfoil were planted in 2-in. pots containing a 1-to-1 sand-peat soil mixture. Each pot held three 3-in.-long cuttings.

39. In test 1, the pots were placed in 5-gal aquaria in the growth room. The temperature was 25 C, light intensity was 80-100 ft-c on a 12-hr photoperiod. Water in the aquaria was replaced every 3 days. After 8 days, appropriate volumes of 2,4-D BEE stock solution were added to the aquaria to bring the concentration to 0.5, 1.0, 2.5, or

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* See ** footnote on p. A12.

5.0 ppmw of 2,4-D. After 0, 1, 2, 4, 8, 16, 24, 48, or 96 hr of contact, the plants were removed from the aquaria, rinsed in running water for 30 min, and then placed in gallon jars in the growth room. Exposure times were replicated three times and consisted of two pots per jar. Because of the number of jars involved; this test was conducted in two parts, 11 days apart. The first part consisted of 1- to 8-hr exposure times, and the second part of 16- to 96-hr exposure times. A second test was conducted in which treatments were applied in outdoor tanks. Three tanks 86 in. long by 30 in. wide by 19 in. deep containing 190 gal of water were used in the test. Potted milfoil plants were placed in the tanks and after 2 weeks, treatments of 0.5, 1.0, or 2.5 ppmw of 2,4-D were applied as previously described. Water temperature at the time of treatment was 18 C. Treatment of the plants, exposure times, and number of replicates were the same as those in the first test. Observations were made at weekly intervals to determine percent herbicidal injury.

Results of test 1

40. As might be predicted, herbicide injury to the plants increased with increasing concentration or exposure time. Water milfoil was destroyed after a 1-hr exposure to a 5-ppmw concentration of 2,4-D (table A11). A 4-hr-exposure period was required at the 2.5-ppmw rate. In one part of the test with the 1.0-ppmw treatment rate, an 8-hr exposure produced adequate control, but in the second part of this test no exposure time was adequate. Not one of the exposure times was adequate at the 0.5-ppmw concentration in these tests.

41. In both the 0.5- and 1.0-ppmw treatments, a difference in plant response was observed between the 8- and 16-hr exposure times. The extent of damage was less for exposure periods of 16 hr or longer than for the 8-hr exposure. The obvious general explanation, considering that the test was separated in time at this point, is that the experimental conditions were altered in some way. Because of the apparent anomalous response of the plants to increasing exposure times

Table A11

Response of Water Milfoil to Increasing Periods of Exposure to Several Concentrations of 2,4-D (Test 1)

Treatment Rates of 2,4-D ppmw	Exposure Time hr	Percent Injury, Weeks After Treatment									
		1	2	3	4	5	6	7	8	9	10
5.0	1	10	17	82	90	93	95	99	100	100	100
	2	17	32	88	95	98	98	100	100	100	100
	4	13	28	92	97	99	99	100	100	100	100
	8	15	37	96	98	99	99	100	100	100	100
	16	12	37	95	98	99	100	100	100	100	100
	24	18	67	99	100	100	100	100	100	100	100
	48	17	80	99	100	100	100	100	100	100	100
	96	20	87	99	100	100	100	100	100	100	100
2.5	1	12	13	20	48	80	87	97	98	98	97
	2	8	15	35	65	88	90	92	93	93	90
	4	17	18	22	77	95	96	99	100	100	100
	8	18	20	78	87	97	97	100	100	100	100
	16	13	25	82	92	94	99	100	100	100	100
	24	10	25	85	92	93	99	100	100	100	100
	48	15	48	95	97	99	100	100	100	100	100
	96	17	50	97	99	100	100	100	100	100	100
1.0	1	6	7	12	12	45	50	67	82	83	77
	2	10	10	17	20	60	67	82	87	90	88
	4	17	15	27	32	68	78	88	93	96	93
	8	17	18	28	38	70	80	95	99	100	100
	16	12	13	27	47	65	72	60	55	55	53
	24	10	17	27	42	70	75	70	65	60	60
	48	12	20	38	67	82	88	85	85	85	85
	96	15	20	57	75	80	90	85	87	87	90
0.5	1	5	5	10	13	27	40	38	42	45	40
	2	5	5	10	18	40	55	62	60	58	57
	4	10	12	18	28	57	58	53	57	55	52
	8	13	13	17	30	63	68	70	73	73	63
	16	10	10	15	32	55	67	65	62	53	55
	24	5	10	17	28	58	70	63	62	58	60
	48	10	12	17	42	70	85	77	73	67	63
	96	13	13	17	37	73	82	68	65	60	60
Controls	Part 1 1-8	0	0	0	2	4	12	12	18	20	20
	Part 2 16-96	0	0	0	0	0	0	2	2	4	6

at these two concentrations, the tests were repeated. The results of the second test are shown in table A12.

Results of test 2

42. In this test, as in the previous test, plant injury increased with both increased herbicide concentrations and exposure times. Maximum injury to water milfoil with the 0.5-ppmw treatment was observed 6 weeks following a 96-hr exposure to the herbicide. The injury rating

Table A12

Response of Water Milfoil to Increasing Periods of Exposure to Several Concentrations of 2,4-D (Test 2)

Treatment Rates of 2,4-D ppmw	Exposure Time hr	Percent Injury, Weeks After Treatment									
		1	2	3	4	5	6	7	8	9	10
0.5	1	5	5	7	10	12	23	25	35	28	28
	2	5	5	8	12	12	32	35	45	40	38
	4	5	8	12	15	17	37	38	45	40	40
	8	5	10	15	27	40	53	60	63	55	53
	16	5	10	15	33	45	58	67	68	63	58
	24	10	12	17	43	58	68	68	73	68	63
	48	12	15	23	45	70	77	68	77	73	70
	96	15	17	28	52	82	88	77	78	77	75
1.0	1	5	5	10	13	17	42	43	53	48	47
	2	7	8	10	17	33	43	42	53	48	48
	4	8	12	15	18	37	43	45	55	53	50
	8	10	13	20	33	50	67	70	67	68	68
	16	10	15	22	48	68	83	87	88	90	92
	24	12	17	25	55	78	88	88	90	90	92
	48	15	18	33	68	93	97	100	100	100	100
	96	17	23	40	82	95	99	100	100	100	100
2.5	1	8	10	13	25	72	78	72	68	55	53
	2	8	12	15	33	78	85	82	82	78	77
	4	10	15	22	53	77	88	87	88	87	90
	8	10	17	33	70	94	97	99	100	100	100
Controls		0	0	0	1	1	1	1	1	1	1

was seen to decrease at later observation periods indicating that regrowth was occurring. The slow rate of increase in the injury rating with increasing exposure time is evidence that the 0.5-ppmw concentration was too low to be effective.

43. The 1.0-ppmw treatment produced a maximum injury and effective control of water milfoil 7 weeks after a 48-hr-exposure period. The 24-hr-exposure period, although producing approximately 90% injury to the plants after 8 weeks, was not adequate as the increase in injury rating beyond this period was too gradual to be significant.

44. The 2.5-ppmw treatment produced 100% injury to the plants 7 to 8 weeks after an 8-hr-exposure period.

45. Under the condition of the second test, 48 hr of contact to 2,4-D BEE applied at the rate of 1.0 ppmw were required for a complete kill of the test plants. Assuming that under these conditions, this is the critical combination of concentration and contact time for 2,4-D and water milfoil, the amount of herbicide required for control is dependent upon the flow rate of water. For example, at a rate of discharge of 1 cubic foot per second (cfs), 86,400 cu ft of water (646,317 gal) would flow past a given point in 24 hr. In 48 hr, 1,292,634 gal or 10,787,419 lb of water would flow past this point. In order to maintain a 1.0-ppmw concentration of the herbicide in this volume of water for 48 hr, approximately 10.8 lb of 2,4-D would be required.

46. Release rate studies on a 30% formulation of 2,4-D BEE in PVC conducted at Edgewood Arsenal during FY 70 revealed that 7.6% of the initial amount incorporated into pellets was released during the first day. The amount released was 11.0% on the third day and 14.8% on the fifth day. This corresponds to rates of 7.6, 3.93, and 2.96% per day, respectively, for the three observations. The average for the three observations is 5.2% per day. Applying this value as an estimate for the release rate figure, 104 lb (0.052 × 104 = 5.4 lb per day) of 2,4-D in a 30% formulation would be required per cubic foot per second

of discharge to maintain a 1.0-ppmw concentration for 48 hr (the 30% designation refers to the concentration of the ester in the formulation which converts to 21%). In order to provide approximately 104 lb of 2,4-D acid, 495 lb of the 30% formulation would be required per cubic foot per second; that is, 0.21 x 495 = 104. At a discharge rate of 100 cfs (not an uncommonly high rate), 49,500 lb of the controlled-release formulation would be required to maintain a 1.0-ppmw concentration over a 24-hr period. These calculations assume that the rate of herbicide release from the carriers is constant. This criterion has not been met to date, as the release rates have been shown to decrease with time. A decreasing release rate would tend to reduce the amount of herbicide released and consequently would reduce the herbicide concentration in water below the critical phytotoxic level.

47. In a flowing water situation, the controlled-release formulations as presently designed would be a prohibitively costly method of controlling water milfoil. This would be true even if it were possible to provide a sustained release of 2,4-D from the formulations beyond 6 or 8 weeks. There may be an advantage in using controlled-release formulations in nonflowing water. The criterion of providing a carrier system with a constant release rate would still apply, however. Critical phytotoxic concentrations in water would still need to be maintained in order to provide control of regrowth or retardation of existing plant growth.

Toxicity of Controlled-Release Formulations to Fish

Methods and materials

48. Before the controlled-release herbicide formulations are field tested, information of potential environmental effects should be obtained. For this reason, an evaluation of the compounds in terms of toxicity to fish is of primary importance.

49. The purpose of this experiment was to determine the toxicity

of various formulations of herbicide on three species of fishes over a period of 7 days. The species selected were bass (Micropterus punctulatus), bluegill (Lepomis macrochirus), and catfish (Ictalurus punctatus).

50. The fish species under investigation were maintained in 3-gal plastic containers at temperatures of 20-22 C with a photoperiod of 12 hr at 80 ft-c. Each herbicide formulation in the bass experiment required 39 containers and two fish per container, except the control which used 16 containers. The bluegill test required four containers for each rate of herbicide and five fish per container, except the control which used 19 containers. The catfish test required four containers with five fish in each container for each rate of herbicide, except the control which used 20 containers.

51. Each formulation was assayed at two rates for the evaluation periods 1, 2, 4, 8, 24, and 48 hr. Evaluations on bass extended through 96 hr and on catfish through 168 hr. The percent mortality was calculated at the end of each individual evaluation period.

52. The controlled-release formulations and rates used were: 11ACE-E, 20% acid equivalent (a.e.) at 5 and 10 ppmw; 14ACE-B, 16.1% a.e. at 5 and 10 ppmw; encapsulated alkyl amine salt of 2,4-D, 22.6% a.e. at 5 and 10 ppmw; Fenac, 21% a.e. at 5 and 10 ppmw; Base 89A (PVC) at 10 and 20 ppmw; and LV-4 (PVC), 13% a.e. at 5 and 10 ppmw.

Bass

53. Data from tests with bass (Micropterus punctulatus) exposed to 5- and 10-ppmw Fenac for a period of 96 hr are presented in table A13. The highest rate of mortality was 1%, which occurred in the controls after 48 hr. There was also 1% mortality after exposure of bass to 10-ppmw Fenac for a period of 8 hr. Because suppliers were unable to provide additional fish for the tests, Fenac was the only compound assayed on bass.

Bluegill

54. The evaluation period for bluegill (Lepomis macrochirus) was

Table A13

Toxicity of Fenac Formulated in PVC on Bass in Still-Water Laboratory Tests

No. of Fish Used	Formulation	Treatment Rate ppmw	Percent Mortality, Hours After Treatment							
			1	2	4	8	24	48	72	96
78	Fenac (PVC)	5	0	0	0	0	0	0	0	0
78	Fenac (PVC)	10	0	0	0	1	1	1	1	1
32	Control		0	0	0	0	0	1	1	1

Note: Fenac toxicity is an average of 39 replicates. The control is an average of 16 replicates.

terminated after 48 hr because the fish tended to feed on the chemical after this period (table A14).

55. Table A14 indicates that the highest mortality of bluegill was 65%, which occurred in the controls. The highest mortality resulting from exposure to the herbicides was 40% from 5 ppmw of the encapsulated alkyl amine after 48 hr. The lowest mortality of bluegill was 13% which resulted from exposure to 10 ppmw of the 14ACE-B and 20 ppmw of the Base 89A after 48 hr.

56. The mortality of 20 bluegills exposed to 5 ppmw of 11ACE-E for the evaluation periods through 8 hr was 0.0%. After 24 hr the mortality was 5%, and after 48 hr 35%.

57. Exposure of 20 bluegills to 10 ppmw of 11ACE-E for the evaluation period through 8 hr resulted in 0.0% mortality. The 24-hr evaluation resulted in 8% mortality. After 48 hr, there was 23% mortality.

58. Of the 20 bluegills exposed to 5 ppmw of LV-4 (PVC), no deaths occurred during the first 8 hr of the test. After 24 hr there was 5% mortality, and after 48 hr 23% mortality.

Table A14

Toxicity of Various Formulations of Herbicides to Bluegill in Still-Water Laboratory

No. of Fish Used	Formulation	Treatment Rate ppmw	Percent Mortality, Hours After Treatment					
			1	2	4	8	24	48
20	11ACE-E	5	0	0	0	0	5	35
20		10	0	0	0	0	8	23
20	LV-4 (PVC)	5	0	0	0	0	5	23
20		10	0	0	0	0	3	23
40	Base 89A (PVC)	10	0	0	0	3	5	25
39		20	0	0	0	0	3	13
40	14ACE-B	5	0	0	0	0	3	18
39		10	0	0	0	3	3	13
40	Fenac	5	0	0	0	0	3	18
40		10	0	0	0	0	8	33
40	Alkyl amine salt (2,4-D encapsulated)	5	0	0	0	0	5	40
40		10	0	0	0	0	0	23
95	Control		0	0	0	1	12	65

Note: Each value is an average of 4 replicates except the control which is an average of 19.

59. Of the 20 bluegills exposed to 10-ppmw LV-4 (PVC), no deaths occurred during the first 8 hr of the test. After 24 hr, there was 3% mortality. After 48 hr, there was 23% mortality.

60. The mortality of 40 bluegills exposed to 10-ppmw Base 89A (PVC) for the evaluation periods through 4 hr was 0.0%. After 8 hr there was 3% mortality; after 24 hr, 5% mortality; and after 48 hr, 25% mortality.

61. Of the 39 bluegills exposed to 20-ppmw Base 89A (PVC) for

the evaluation period through 8 hr, there were no deaths. The 24-hr exposure resulted in 3% mortality. After 48 hr there was 13% mortality.

62. The mortality of 40 bluegills exposed to 5-ppmw 14ACE-B for the evaluation periods through 8 hr was 0.0%. There was 3% mortality after 24 hr and 18% mortality after 48 hr.

63. Of the 39 bluegills exposed to 10-ppmw 14ACE-B for the period through 4 hr, there were no deaths. After 8 hr, there was 3% mortality. The 24-hr exposure resulted in 3% mortality. After 48 hr, there was 13% mortality.

64. The mortality of 40 bluegills exposed to 5-ppmw Fenac for the evaluation periods through 8 hr was 0.0%. There was 3% mortality after 24 hr and 18% mortality after 48 hr.

65. Of the 40 bluegills exposed to 10-ppmw Fenac for the period through 8 hr, there were no deaths. After 24-hr exposure there was 8% mortality and after 48-hr, 33% mortality.

66. The mortality of 40 bluegills exposed to 5-ppmw of the alkyl amine for the evaluation period through 8 hr was 0.0%. There was 5% mortality after 24 hr and 40% mortality after 48 hr.

67. Of the 40 bluegills exposed to 10-ppmw of the alkyl amine for the period through 24 hr, there were no deaths. After 48 hr, there was 23% mortality.

68. The mortality of 95 bluegills in the control for the evaluation period through 4 hr was 0.0%. There was 1% mortality after 8 hr. After 24-hr exposure there was 12% mortality and after 48-hr, 65% mortality.

Catfish

69. The exposure period for catfish (*Ictalurus punctatus*) was terminated after the 168-hr evaluation.

70. Data from tests of catfish indicate the highest mortality was 25% which occurred in the fish exposed to 5-ppmw Fenac for a period of 168 hr (table A15). The lowest mortality of catfish was 0.0% which resulted from exposure for 168 hr to 5-ppmw 14ACE-B, 10-ppmw LV-4 (PVC),

Table A15

Toxicity of Various Formulations of Herbicides to Catfish in Still-Water Laboratory Tests

No. of Fish Used	Formulation	Treatment Rate ppmw	Percent Mortality, Hours After Treatment								
			1	2	4	8	24	48	72	96	168
20	11ACE-E	5	0	0	0	0	0	10	10	10	10
20		10	0	0	0	0	10	18	18	18	18
40	LV-4 (PVC)	5	0	0	0	0	8	8	8	8	8
40		10	0	0	0	0	0	0	0	0	0
40	Base 89A (PVC)	10	0	0	0	0	5	10	13	13	13
40		20	0	0	0	0	18	20	23	23	23
40	14ACE-B	5	0	0	0	0	0	0	0	0	0
40		10	0	0	0	0	0	13	13	13	13
40	Fenac	5	0	0	0	0	5	13	13	15	25
40		10	0	0	0	0	18	18	18	23	23
40	Alkyl amine salt (encapsulated)	5	0	0	0	0	13	13	13	13	13
40		10	0	0	0	0	0	0	0	0	0
96	Check		0	0	0	0	6	16	16	18	22

Note: Each value is an average of 4 replicates, except the control which is an average of 19.

and 10-ppmw of the alkyl amine.

71. There were no deaths of the 20 catfish exposed to 5-ppmw 11ACE-E for the evaluation period through 24 hr. There was 10% mortality for the 48-, 72-, 96-, and 168-hr exposures.

72. Of the 20 catfish exposed to 10-ppmw 11ACE-E for the periods through 8 hr there was 0.0% mortality. There was 10% mortality after 24 hr. After 48 hr and through 168 hr there was 18% mortality.

73. Of the 40 catfish exposed to 5-ppmw LV-4 (PVC) for the period

through 8 hr there was 0.0% mortality. For the period 24 hr through 168 hr there was 8% mortality.

74. Of the 40 catfish exposed to 10-ppmw LV-4 (PVC) for the period through 168 hr there were no deaths.

75. The mortality of 40 catfish exposed to 10-ppmw Base 89A (PVC) for the period through 8 hr was 0.0%. There was 5% mortality after 24 hr. After 48 hr there was 10% mortality. For the period 72 hr through 168 hr there was 13% mortality.

76. Of the 40 catfish exposed to 20-ppmw Base 89A (PVC) for the period through 8 hr there were no deaths. There was 18% mortality after 24 hr. After 48 hr there was 20% mortality. For the period 72 hr through 168 hr the mortality rate was 23%.

77. The mortality of 40 catfish exposed to 5-ppmw 14ACE-B for the period through 168 hr was 0.0%.

78. Of the 40 catfish exposed to 10-ppmw 14ACE-B for the period through 24 hr there were no deaths. For the period 48 hr through 168 hr the mortality rate was 13%.

79. The mortality of 40 catfish exposed to 5-ppmw Fenac for the period through 8 hr was 0.0%. After 24 hr there was 5% mortality. For the period 48 hr through 72 hr there was 13% mortality, after 96 hr there was 15% mortality, and after 168 hr there was 25% mortality.

80. Of the 40 catfish exposed to 10-ppmw Fenac for the period through 8 hr there were no deaths. For the period 24 hr through 72 hr there was 18% mortality. For the period 96 hr through 168 hr there was 23% mortality.

81. The mortality of 40 catfish exposed to 5-ppmw of the alkyl amine for the period through 8 hr was 0.0%. For the period 24 hr through 168 hr there was 13% mortality.

82. Of the 40 catfish exposed to 10 ppmw of the alkyl amine for the period of 1 hr through 168 hr, there were no deaths.

83. The mortality of the 96 catfish exposed to the control for the period through 8 hr was 0.0%. After 24 hr, there was 6% mortality.

For the period 48 hr through 72 hr there was 16% mortality. After 96 hr there was 18% mortality. After 168 hr there was 22% mortality.

Conclusions and discussion

84. The 5-ppmw rate of 11ACE-E, the 10-ppmw rate of Fenac, and the 5-ppmw rate of alkyl amine resulted in 33% to 40% mortality to bluegills after 48-hr exposure. The lowest percentage of mortality resulted from the 20-ppm Base 89A (PVC).

85. The highest mortalities of catfish were 25% and 23% which resulted from 168-hr exposure to 5-ppmw Fenac and from 72-hr exposure to 20-ppmw Base 89A (PVC), respectively. The lowest mortality was 0.0% which resulted from 168-hr exposure to 5-ppmw 14ACE-B, 10-ppmw LV-4, and 10-ppmw alkyl amine salt.

86. Bass, after 8-hr exposure to 10-ppmw Fenac, had 1% mortality. This indicated that bass and bluegill are similarly susceptible to Fenac.

87. Catfish, however, showed no toxicity to Fenac until after an exposure of 24 hr. This indicated that bass and bluegill were more affected by the Fenac treatment.

88. Several factors could influence the levels of toxicity. One obvious factor is the toxicity of the chemical involved. Another factor is the material which encapsulates the time-release herbicides. Due to the lack of knowledge concerning the use of such material as PVC for capsules, there may be factors influencing toxicity which have not been recognized.

89. None of the formulations appeared to be toxic to the test fish under the conditions of these tests. At no point in the evaluation did the mortality of the treated fish appear significantly higher than the fish in the controls.

Suggestions for further study

90. Suggestions for further study are as follows:

- a. Correlation of herbicide concentration levels in the aquatic environment with those levels present in the tissue of the fish population.

b. Influence of herbicides on the reproduction of bass, bluegill, and catfish.

c. Effect of herbicides on the rate of growth of bass, bluegill, and catfish.

APPENDIX B

EVALUATION OF SLOW-RELEASE HERBICIDE FORMULATIONS FOR AQUATIC WEED CONTROL

U. S. Army Environmental Hygiene Agency
Edgewood Arsenal
Aberdeen Proving Ground, Md.

EVALUATION OF SLOW-RELEASE HERBICIDE FORMULATIONS FOR AQUATIC WEED CONTROL*

by

Larry M. Nelson**

1. REFERENCES.

a. Memorandum of Intra-Agency Agreement between U. S. Army Environmental Hygiene Agency and the Office, Chief of Engineers, 15 October 1968.

b. Entomological Special Study No. 31-004-69/71, Evaluation of Controlled Release Herbicide Formulations for Aquatic Weeds July 1969-July 1970, transmitted 23 October 1970.

2. PURPOSE.

The objectives of this investigation were as follows:

a. Determine the concentrations of Fenac® (2,3,6-trichlorophenoxyacetic acid), butoxyethanol ester of 2,4-dichlorophenoxyacetic acid (2,4-D BEE), and alkanolamine salts of 2,4-dichlorophenoxyacetic acid (2,4-D) maintained in water in the laboratory when formulated in polyvinyl chloride plastisols (PVC), or biodegradable rubber, or when encapsulated.

b. Provide laboratory support to the U. S. Department of Agriculture, Field Plantation Laboratory, Fort Lauderdale, Fla. (hereafter referred to as USDA, Fort Lauderdale), by conducting residue analysis of water samples from outdoor pool tests of slow-release herbicide formulations.

c. Formulate herbicides in PVC in sufficient quantities for limited outdoor pool testing and develop a slow-release formulation of Diquat® (6,7-dihydrodipyrido [1,2a:2',1'c] pyrazinedium salts) suitable for preliminary laboratory bioassay studies.

3. GENERAL.

a. Earlier investigations (ref para 1b) demonstrated the feasibility of aquatic weed control using polymer carriers under laboratory conditions. It was a recommendation of these investigations (ref para

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* Contribution of U. S. Army Environmental Hygiene Agency, Edgewood Arsenal, Aberdeen Proving Ground, Md.

** Captain MSC, Entomologist, Entomology Sciences and Pesticides Division.

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1b) that release rate studies of various herbicides from PVC and biodegradable rubber formulations be conducted in the laboratory. The report further recommended that new experimental formulations should be developed and tested in the laboratory and that cooperative field studies with USDA, Fort Lauderdale, be initiated.

b. Laboratory release rate studies of various herbicides in PVC, biodegradable rubber, and encapsulated formulations were conducted.

c. Cooperative studies with USDA, Fort Lauderdale, were initiated, wherein this Agency provided laboratory support for field studies.

d. Experimental quantities of herbicides in PVC were produced in the laboratory and a new experimental formulation of Diquat was obtained commercially.

4. METHODS AND MATERIALS.

a. Laboratory Release Rate Studies.

(1) Release rates of Fenac and 2,4-D BEE from PVC formulations into water were determined under static laboratory conditions. Degradation rates of technical Fenac, technical 2,4-D BEE, and 2,4-D BEE emulsifiable concentrate (e.c.) were also determined. Basic components of the PVC plastisol formulations were the resin Geon® 135 and the plasticizer di-(2-ethylhexyl) phthalate (plasticizer:resin 1:1). Formulations evaluated are shown in table B1.

Table B1

Herbicide PVC Formulations

Herbicide*	Herbicide %	Herbicide a.e.** %	Resin %	Plasticizer %
Fenac	30	21	35	35
89A 2,4-D BEE	30	21	35	35
LV-4 2,4-D BEE	30	13	35	35
Control	--	--	50	50

* Technical Fenac (70% a.e.); technical 89A 2,4-D BEE (70% a.e.); and Weedone® LV-4 2,4-D BEE emulsifiable concentrate (43.3% a.e.). Furnished by Amchem Products, Inc., Ambler, Penn.

** Acid equivalent.

(2) Formulations were made according to the following procedures: the herbicide and plasticizer were added to the Geon 135 resin and the mixture stirred. The premixed plastisols were poured into aluminum molds and thermally cured at 120-125 C for 30 min. The resulting pellets had an average weight of 65 mg and a density >1.00.

(3) Release rates of 2,4-D BEE from biodegradable rubber formulations into water were also determined under static laboratory conditions. Formulations were developed by the Creative Biology Laboratory, University of Akron, Akron, Ohio, and forwarded to this Agency for evaluation. Formulations tested are shown in table B2.

Table B2

Herbicide-Biodegradable Rubber Formulations

Herbicide*	Formulation	Herbicide a.e. %	Density
2,4-D BEE	11ACE-C	8.6	<1.00
	11ACE-E chunk	21.8	>1.00
	11ACE-E ground	20.3	>1.00
	11ACE-J	7.5	>1.00
	11ACE-L	9.7	>1.00
	14ACE-A	22.2	<1.00
	14ACE-B	16.1	<1.00
	15ACE-B(L)	37.5	>1.00
Control	16ACE-A**	--	<1.00
	17ACE-A†	--	<1.00

* Formulated by Creative Biology Laboratory, Akron, Ohio.
** Control for 11ACE series.
† Control for 14ACE and 15ACE series.

(4) Release rate of alkanolamine salts of 2,4-D from an encapsulated formulation was determined under static laboratory conditions. The formulation was provided by the 3M Company, St. Paul, Minn. Composition of the shell material is a mixture of polyethylene, hydrocarbon resin, and paraffin wax. The formulation contains 22.6% acid equivalents (a.e.) alkanolamine salts of 2,4-D and has a density >1.0.

(5) All formulations were evaluated in gallon glass jars containing 3 liters of tap water. The dose rate for all formulations tested was 10.0 ppm a.e. of herbicide. Technical Fenac was applied as an acetone solution. The jars were sealed with aluminum foil liners and screw-cap lids to minimize loss of water due to evaporation. Each formulation was replicated three times. Pellets containing no herbicide served as controls.

(6) Water temperature, pH, and 10-ml water samples for residue analysis were taken weekly through 8 weeks. Water samples were extracted by alkalization, acidification, and chloroform partitioning. Chloroform extracts were then evaporated to dryness and methylated with boron trifluoride-methanol reagent. Appropriate volumes of Nanograde® hexane were added and the methyl esters of Fenac and 2,4-D BEE were then analyzed by gas chromatography.

(7) A Tracor® Model MT-150 gas chromatograph equipped with a Ni^{63} electron capture detector was used for analysis of samples. The instrument was fitted with a 182.88-cm by 0.635-cm glass column packed with Chromosorb® W 80/90 mesh coated with 3% OV-1. The operating parameters were: oven temperature (temp) 200 C; inlet temp 235 C, outlet temp 240 C; detector temp 265 C; attenuation 10^2 by 16; carrier gas N_2; column flow rate 70 cc/min; and chart speed 0.318 cm/min. Percent recovery of known quantities of Fenac, 2,4-D BEE and the alkanolamine salts of 2,4-D using the extraction above, methylation, and analytical procedures were 98.0% for Fenac, 75.0% for 2,4-D BEE, and 89.0% for the alkanolamine salts of 2,4-D.

b. Outdoor Pool Tests - Residue Analysis.

(1) Outdoor pool tests were conducted by USDA, Fort Lauderdale, during the period June through August 1970 for control of eurasian water milfoil using a 30% active ingredient (a.i.) 2,4-D BEE-PVC formulation prepared by this Agency (ref para 1b) and a commercial clay granule formulation containing 20% a.i. 2,4-dichlorophenoxyacetic acid (2,4-D). The 2,4-D BEE-PVC formulation was tested at dose rates of 1, 2, and 4 ppm. The 2,4-D clay granule was tested at 1 and 2 ppm. Water samples for residue analysis were taken at 1, 4, and 7 days and biweekly thereafter through 8 weeks. Untreated pools served as controls and each treatment was replicated three times. Water samples were extracted with chloroform at USDA, Fort Lauderdale, and the extracts forwarded to this Agency for residue analysis. Upon receipt of samples, the chloroform was evaporated, samples were methylated, and the methyl ester of 2.4-D analyzed by gas chromatography as previously described (see para 4a(6) and (7)).

(2) A second series of outdoor pool tests using slow-release herbicide formulations against eurasian water milfoil were conducted

by USDA, Fort Lauderdale, from October 1970 to October 1971. Formulations evaluated were 30% Fenac in PVC, 30% Weedone LV-4, 2,4-D BEE in PVC, 30% 89A 2,4-D BEE in PVC (table B1), 11ACE-E and 14ACE-B biodegradable rubber formulations of 2,4-D BEE (table B2), and encapsulated alkanolamine salts of 2,4-D (para 4a(4)). Dose rates for the 30% 89A 2,4-D BEE-PVC formulation were 10.0 and 20.0 ppm a.e. All other formulations tested were dosed at 5.0 and 2.5 ppm a.e. Water samples for residue analysis were taken at 1 and 4 days, weekly 1-4 weeks, biweekly 4-10 weeks, and monthly 10-46 weeks after treatment. Untreated pools served as controls. Each treatment was replicated three times. Water samples were extracted at USDA, Fort Lauderdale, and the chloroform extracts forwarded to this Agency for residue analysis. Upon receipt of samples, the chloroform was evaporated, samples were methylated and the methyl ester of 2,4-D analyzed by gas chromatography as previously described (see para 4a (6), (7)).

c. Experimental Formulations.

(1) Polymer formulations of technical Fenac (70% a.e.), technical Base 89A 2,4-D BEE (70% a.e.), Weedone LV-4 emulsifiable concentrate 2,4-D BEE (43.3% a.e.), and analytical grade 2,4-D* (100% a.e.) were produced in test quantities at this Agency. Basic components of the formulations were the resin Geon 135 and the plasticizer di-(2-ethylhexyl) phthalate (resin:plasticizer 1:1) (table B3). Formulations were made according to procedures previously described (para 4a(2)). Formulations were forwarded to USDA, Fort Lauderdale, for biological evaluations.

Table B3

Experimental Formulations

Herbicide	Herbicide %	Herbicide a.e. %	Resin %	Plasticizer %	Laboratory Quantity, g
89A 2,4-D BEE	30	21	35	35	1200
LV-4 2,4-D BEE	30	13	35	35	1475
Fenac	30	21	35	35	1300
2,4-D	30	30	35	35	32

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* Furnished by Dow Chemical Company, Midland, Mich.

(2) At the request of Dr. Edward O. Gangstad, Chief, Aquatic Plant Control, Corps of Engineers, Washington, D. C., a 400-g sample of 30% Fenac in PVC was forwarded to Dr. Sigmond L. Solymosy, University of Southwestern Louisiana, Lafayette, for testing.

(3) A formulation of Diquat was obtained from GAF Corporation, Hagerstown, Md., for biological evaluations. The formulation was composed of 10%, by weight, of Diquat in a solution of silicate and water on a mineral base granule. The formulation was forwarded to USDA, Fort Lauderdale, for testing.

5. RESULTS AND DISCUSSION.

a. Laboratory Release Rate Studies

(1) Results of release rate studies of 2,4-D BEE and Fenac from PVC are indicated in figs. B1 and B2. Average residues, along with the minimum and maximum residues detected from each PVC formulation over

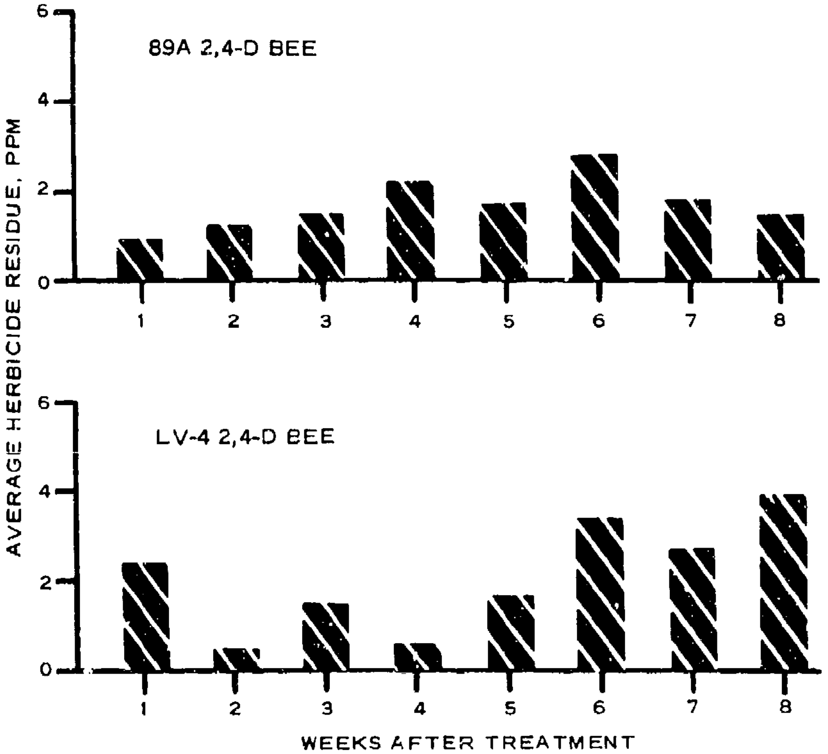

Fig. B1. Release of 89A 2,4-D BEE and LV-4 2,4-D BEE from PVC

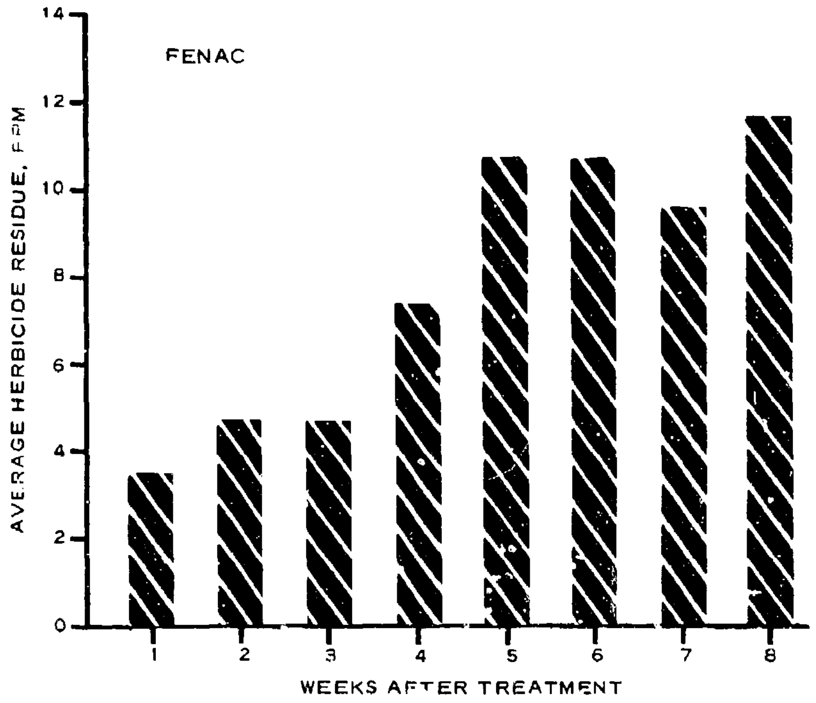

Fig. B2. Release of Fenac from PVC

the 8-week testing period, are shown in table B4. Residues of technical Fenac remained constant from the initial dose rate of 10.0 ppm with an average residue detected over the test period of 11.21 ppm. Residues of

Table B4

Average 2,4-D BEE and Fenac Residues Detected from PVC Formulations*

	Minimum Residue		Maximum Residue		8-Week Avg Residue
Formulation	ppm	Observed At	ppm	Observed At	ppm
Fenac PVC	3.40	Week 1	11.37	Week 8	7.67
89A 2,4-D BEE PVC	0.88	Week 1	2.72	Week 6	1.65
LV-4 2,4-D BEE PVC	0.57	Week 2	3.88	Week 8	2.07

* Sensitivity of method, 0.01 ppm.

technical 89A 2,4-D BEE declined from the initial concentration of 10.0 ppm to 3.73 ppm after 8 weeks with an average residue detected of 6.37 ppm. Residues of LV-4 emulsifiable concentrate 2,4-D BEE declined from the initial concentration of 10.0 ppm to 4.14 ppm after 8 weeks with an average residue over the test period of 6.86 ppm. Water pH and temperature remained constant throughout the test period. Average pH and temperatures measured were pH 5.3 and 23.8 C, respectively.

(2) Results of release rate studies of 2,4-D BEE biodegradable rubber formulations are indicated in figs. B3-B6. Average residues detected in each treatment along with the maximum and minimum residues

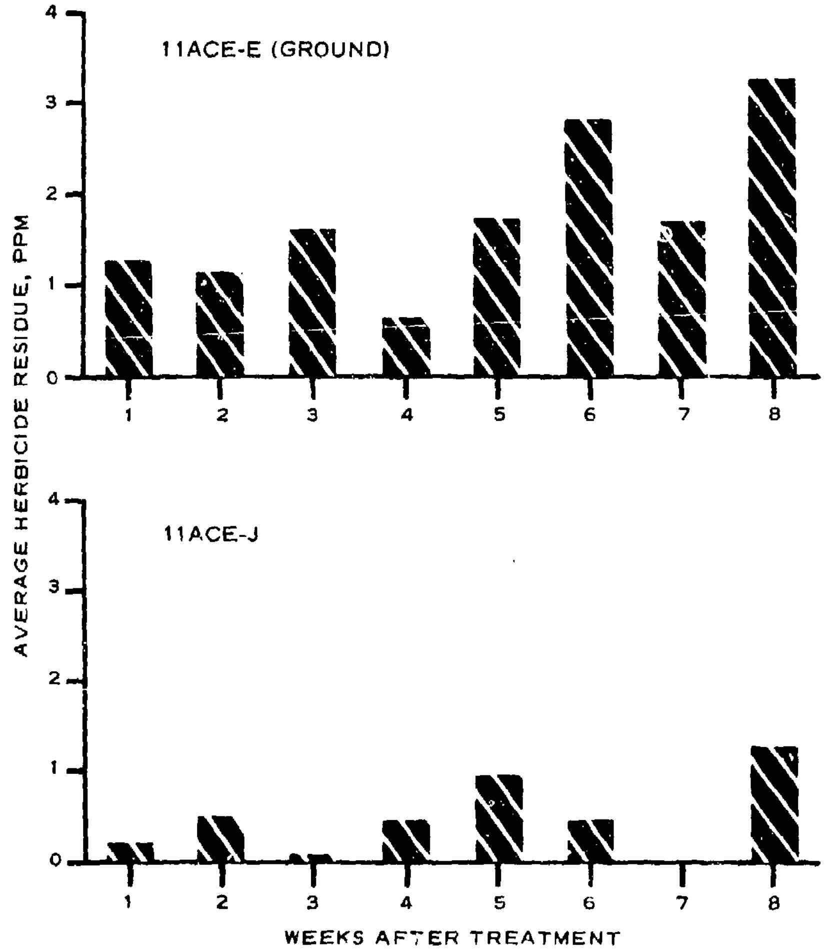

Fig. B3. Release of 2,4-D BEE from biodegradable rubber formulations, 11ACE (ground) and 11ACE-J

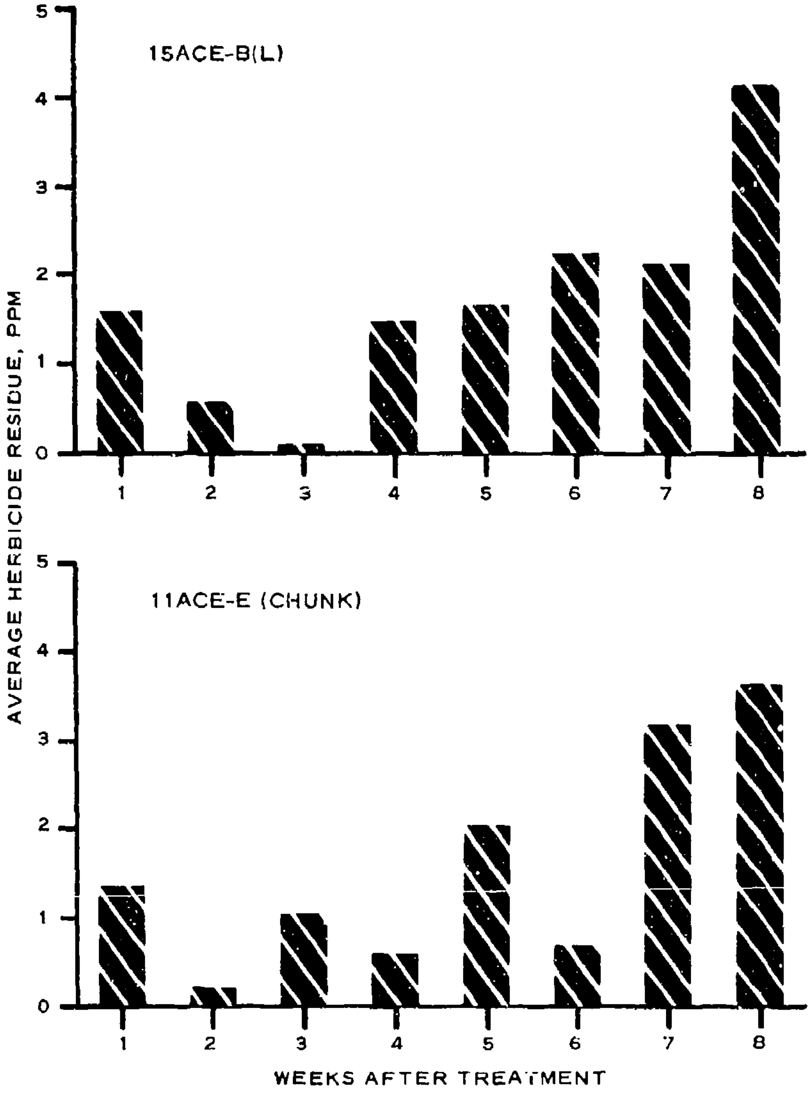

Fig. B4. Release of 2,4-D BEE from biodegradable rubber formulation, 15ACE-B(L) and 11ACE-E (chunk)

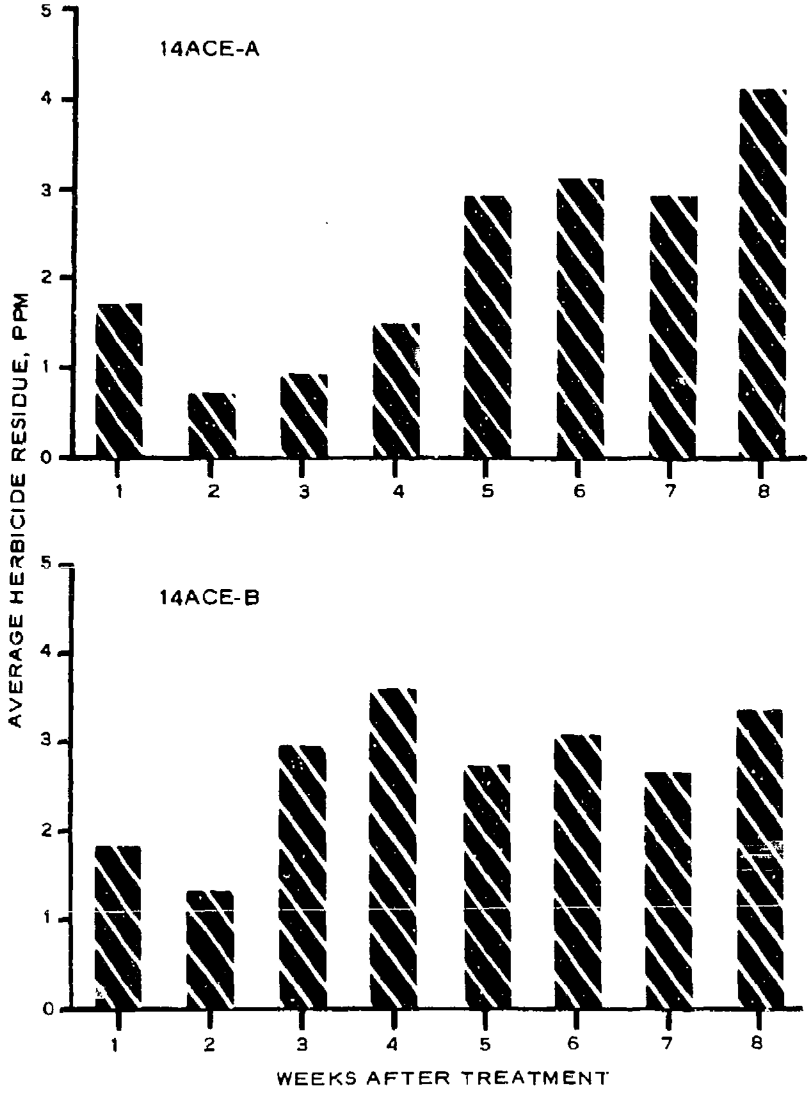

Fig. B5. Release of 2,4-D BEE from biodegradable rubber formulations, 14ACE-A and 14ACE-B

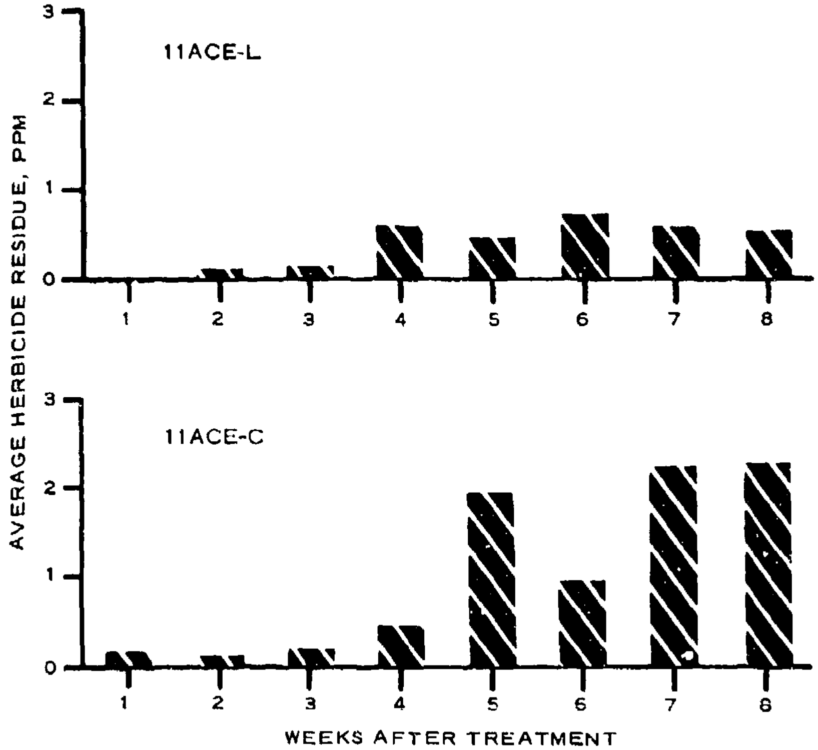

Fig. B6. Release of 2,4-D BEE from biodegradable rubber formulations, 11ACE-L and 11ACE-C

over an 8-week testing period are indicated in table B5. The 11ACE series (11ACE-C, 11ACE-E, 11ACE-J, and 11ACE-L) released at a slower rate than did the 14ACE series (14ACE-A and 14ACE-B) and 15ACE-B(L).

(3) Results of release rate tests using an encapsulated alkanolamine salts of 2,4-D formulation are found in fig. B7. Over the 8-week test period, the lowest residue detected was 0.19 ppm, occurring at 1 week, and the highest residue was 3.10 ppm at 2 weeks, while the average over the entire test period was 1.64 ppm.

b. Outdoor Pool Tests - Residue Analysis.

(1) Results of residue analysis of pool tests conducted June-August 1970 are found in table B6. Average residues maintained over 6 weeks from the 30% 2,4-D BEE PVC formulation were 0.041 ppm for the 1-ppm dose rate, 0.078 ppm for the 2-ppm dose rate, and 0.182 for the 4-ppm dose rate. Residues measured in 2,4-D attaclay granule treatments average 0.298 ppm for the 1-ppm dose rate and 0.708 ppm for the 2-ppm dose rate over 6 weeks. No residues were detected in the control

Table B5

Average 2,4-D BEE Residues Detected from Biodegradable Rubber Formulations*

Formulation	Minimum Residue ppm	Minimum Residue Observed At	Maximum Residue ppm	Maximum Residue Observed At	8-Week Avg Residue ppm
11ACE-C	0.07	Week 2	2.24	Week 8	1.02
11ACE-E chunk	0.20	Week 2	3.63	Week 8	1.59
11ACE-E ground	0.64	Week 4	3.26	Week 8	1.77
11ACE-J	<0.01	Week 7	1.28	Week 8	0.49
11ACE-L	<0.01	Week 1	0.70	Week 6	0.37
14ACE-A	0.73	Week 2	4.14	Week 8	2.25
14ACE-B	1.33	Week 2	3.62	Week 4	2.72
15ACE-B(L)	0.16	Week 3	4.16	Week 8	1.77

* Sensitivity of method, 0.01 ppm.

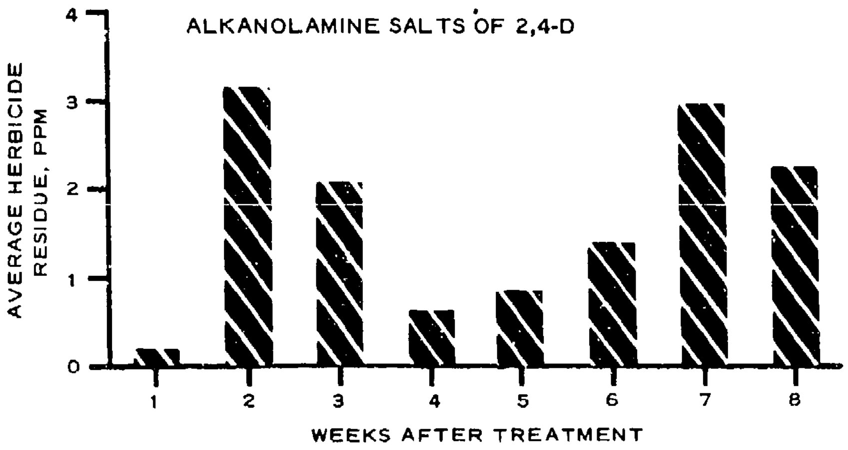

Fig. B7. Release of alkanolamine salts of 2,4-D from an encapsulated formulation

Table B6

Residue Analysis of Outdoor Pool Tests (Average ppm*)

2,4-D BEE and Attaclay

Formulation	Dose Rate ppm	Day 1	Day 4	Week 1	Week 2	Week 4	Week 6	Week 8
2,4-D BEE PVC	1	0.040	0.066	0.094	0.064	0.003	0.001	<0.001
	2	0.079	0.101	0.284	<0.001	<0.001	0.005	<0.001
	4	0.132	0.356	0.531	0.070	0.001	0.003	<0.001
2,4-D attaclay	1	0.400	0.421	0.566	0.103	<0.001	0.002	<0.001
	2	0.680	0.890	0.850	0.412	<0.001	<0.001	<0.001
Control	--	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

* Limit of sensitivity of method, 0.001 ppm.

treatments throughout the test period and no residues were detected in any of the samples 8 weeks after treatment. The data indicate that a 30% 2,4-D BEE PVC formulation is no more effective than a 2,4-D attaclay granule formulation when evaluated at comparable dose rates.

(2) Results of residue analysis of pool tests conducted October 1970-August 1971 are found in tables B7 and B8. Residues of Fenac were detected throughout the 46-week test period. Average residues of Fenac maintained over the test period were 0.795 ppm for the 2.5-ppm dose rate and 1.883 ppm for the 5.0-ppm dose rate. Residues from all other formulations tested were <0.001 ppm 4-10 weeks after treatment. No residues were detected in control pools. With the exception of the Fenac PVC formulation, all formulations tested appear to be similar in overall efficacy.

6. CONCLUSIONS.

a. Fenac PVC and 2,4-D BEE PVC formulations were both effective in maintaining residues in water in the laboratory over an 8-week testing period. However, due to the potential hazard of polychlorinated biphenyl (PCB) contamination of the environment resulting from the use of PVC plastisol formulations, an alternative carrier should be found for use with Fenac.

Table B7

Residue Analysis of Outdoor Pool Tests (Average ppm*) 11ACE-B, 11ACE-E, and Alkanolamine Salts of 2,4-D

Days/Weeks Post Treatment	Dose Rate - ppm a.i.					
	11ACE-B		11ACE-E		Alkanolamine Salts of 2,4-D	
	2.5	5.0	2.5	5.0	2.5	5.0
1 day	0.027	0.149	0.042	0.303	0.018	0.051
4 days	0.055	0.385	0.053	0.402	0.024	0.056
1 week	0.068	0.234	0.291	0.584	0.050	0.157
2	0.015	0.423	0.041	0.861	0.003	0.020
3	0.017	0.040	<0.001	0.038	0.001	0.032
4	0.029	0.043	<0.001**	0.030	<0.001	0.009
6	<0.001	<0.001	<0.001	<0.001	<0.001	0.008
8	<0.001	0.024	<0.001	<0.001	0.004	0.016
10	<0.001	<0.001	<0.001	<0.001	0.009	0.007
14	†	<0.001	†	†	<0.001	<0.001
18		†			<0.001	<0.001
22					†	†

* Sensitivity of method 0.001 ppm.

** Samples leaked in shipment.

† Sampling terminated.

b. The 2,4-D BEE biodegradable rubber formulations maintained residues in water in the laboratory over the test period. However, the 11ACE series was much less effective than was the 14ACE series of formulations. As a result, no further evaluations should be conducted using 2,4-D BEE PVC formulations or the 11ACE series of biodegradable rubber formulations against water milfoil. However, the 14ACE series should be further evaluated against a variety of aquatic weeds.

c. In laboratory tests, the encapsulated formulation of the alkanolamine salts of 2,4-D maintained residues throughout the test period and should be considered for further evaluations in the field.

Table B8

Residue Analysis of Outdoor Pool Tests (Average ppm*)

LV-4 2,4-D BEE PVC, 89A 2,4-D BEE PVC, and Fenac PVC

Days/Weeks Post Treatment	Dose Rate - ppm a.i.					
	LV-4 2,4-D BEE PVC		89A 2,4-D BEE PVC		Fenac PVC	
	2.5	5.0	10.0	20.0	2.5	5.0
1 day	0.043	0.056	0.365	0.402	0.275	1.158
4 days	0.050	0.196	0.447	1.647	0.444	2.076
1 week	0.198	0.480	0.509	1.664	0.860	1.680
2	0.059	0.154	0.235	2.231	0.627	2.591
3	0.015	<0.001	0.002	0.169	0.109	0.726
4	<0.001**	0.006	0.009	0.080	1.414	3.740
6	<0.001	<0.001	<0.001	<0.001	0.605	3.650
8	<0.001	<0.001	<0.001	<0.001	0.780	4.150
10	<0.001	<0.001	<0.001	<0.001	1.860	1.740
14	†	†	†	†	1.062	2.467
18					1.315	1.696
22					1.082	2.630
26					0.721	1.281
30					1.394	1.534
34					0.524	1.491
38					0.303	0.359
42					0.556	0.454
46					0.380	0.480

* Sensitivity of method 0.001 ppm.
** Samples leaked in shipment.
† Sampling terminated.

d. In outdoor pool tests, a Fenac PVC formulation was the most effective in maintaining residues beyond 10 weeks after treatment. The encapsulated alkanolamine salts of 2,4-D formulation produced residues through 10 weeks in the outdoor pools. All other formulations evaluated outdoors were only effective for periods up to 4 weeks.

APPENDIX C

DEVELOPMENT OF SLOW-RELEASE HERBICIDE MATERIALS FOR CONTROLLING AQUATIC PLANTS

Creative Biology Laboratory
University of Akron
Akron, Ohio

DEVELOPMENT OF SLOW-RELEASE HERBICIDE MATERIALS FOR CONTROLLING AQUATIC PLANTS*

by

Suzanne Bille, S. Zachary Mansdorf, and Nathan F. Cardarelli**

Summary

Slow-release formulations of the butoxyethanol ester of 2,4-dichlorophenoxyacetic acid were prepared and evaluated. This herbicide was found to have a relatively high solubility' in natural rubber and only slight solubility in several other elastomeric substances. Loss rate was adjustable by compounding techniques.

In order to release the control agent in the photozone of interest, five product designs were developed. These consisted of floating and sinking pellets, timed release pellets, and top-suspending and bottom-suspending ribbons.

Initial indoor and outdoor evaluations were conducted using four aquatic weeds: water hyacinth, alligator weed, elodea, and eurasian water milfoil.

Top suspenders applied at a rate of 1-ppmw active agent destroyed water hyacinths within 4 weeks of the treatment date in outdoor pool tests. Floating and sinking pellets were ineffectual, even at higher dosages, against this plant. However, all forms of the slow-release formulation controlled milfoil. The butyoxyethanol ester of 2,4-D is not particularly effective against elodea or alligator weed.

The advantage of slow-release formulations lies in their economy of use. One treatment can conceivably provide weed control for several years. Half-lives in excess of 9 months are predicted. Sinking pellets are shown to release 2,4-D at the watercourse bottom with fairly rapid upward dispersion, reading near equilbrium (no gradient) in a short time. In

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* Contract No. DACW73-70-C-0030, Aquatic Plant Control Program, Planning Division, Office, Chief of Engineers, Washington, D. C.

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contrast, floating pellets release at the surface with little downward dispersion of the toxicant.

Formulation 14B, prepared as a suspender, has shown greatest efficacy against water hyacinth. Small factory lots have been prepared of the best suspender, sinker, and floater, and an initial manufacturing analysis has been performed. Field test studies have been initiated in Louisiana with several of the superior materials.

PART I: INTRODUCTION

1. Control of water weeds is a major world problem. Plant infestations severely hamper agriculture dependent upon irrigation in many areas of the world. In the United States growing and decaying plants block navigable waterways, interfere with drainage systems, and often serve as foci of pest insects and other undesirable life forms. Present control methods depend upon mechanical harvesting or the use of herbicides and perhaps, in the future, on biological control. In any case, conventional treatment methodology is economically unattractive and to some degree furthers, directly or indirectly, environmental contamination.

2. The use of slow-release materials may well permit the destruction of the plant at its youngest stage where intoxication levels are lowest and thus reduce the overall contamination problem. A complementary concept advanced by the U. S. Army Corps of Engineers is to release the toxicant in the phytozone of attack, i.e., in the watercourse bottom strata for rooted weeds, or in the first foot of depth for floating plants, and so on. This method should likewise reduce the total amount of toxic agent needed for a given control problem.

PART II: BACKGROUND

3. In 1964 the senior author successfully added various organotin toxicants to rubber matrices and, through certain compounding techniques, caused their slow release into an aquatic environment. The release mechanism is based upon a diffusion-dissolution phenomenon whereby the toxic molecules soluble in the specific polymeric base material slowly migrate toward the pellet surface and then pass into the elastomer-water interface. As dissolution occurs, a solution pressure differential exists, and the natural principle of solution equilibrium sustains the toxicant diffusion.[1]

4. The initial use of "biocidal rubber" lay in marine fouling control.[1,2] Here relatively small amounts of toxicant, less than 8%, by weight, are slowly released from protective rubber sheeting, effectively preventing fouling over a period of time measured in years.[2] Practical applications followed[3] and methods of increasing or decreasing loss rates were developed.[4,5,6] The efficacy of the now commercially available product has been reported in the technical and trade literature.

5. In 1968 the iso-octyl ester of 2,4-D and other herbicides were formulated in slow-release chloroprene recipes at The University of Akron. Laboratory tests against the water hyacinth (mature plant) indicated continuous and effective toxicant release over several months. No definitive experimentation was performed, but rather a pilot qualitative study to assess the potential of this technique in water weed control.

PART III: PROJECT GOALS

6. The first-year program encompassed the development of slow-release herbicide materials active in the phytozone of interest. Originally, the butoxyethanol ester (BEE) and the dimethylamine (DMA) of 2,4-dichlorophenoxyacetic acid were selected as toxicants. Five concepts keyed to phytozone release, sinkers, floaters, suspenders, time-release floaters, and "bouquets," were advanced.

7. Formulations were to be prepared in accordance with the compounders art, with an eye toward economy in materials and processing costs, and evaluated under laboratory conditions against four aquatic weeds, emphasizing the water hyacinth (Eichhornia crassipes). Both indoor and outdoor tests in small plastic pools were planned. Instrumental analysis of herbicide release rates were to be performed to establish efficacy of the concept and back up bioassay results. Screening tests would permit the selection of superior candidates (phase I); these materials would be modified (phase II) as necessary to achieve maximum results. The modified materials would then be shipped in appropriate quantities to laboratory and field test sites selected by the contracting agency.

8. Phase II evaluations were continued through the second year. Small-scale field test and confirmance studies at the U. S. Department of Agriculture laboratory (Fort Lauderdale, Fla.) were initiated with Plant Development Laboratory supplying quantities of the better formulations.

PART IV: PREPARATORY ACTIVITIES

Plant Propagation

9. A number of 10-ft diam (2.5-ft depth) and 8-ft diam (2-ft depth) tanks were set up in which to grow water plants. The tanks were vinyl "swimming pools" supported within a sheet-metal cylinder. A soil mix of locally procured topsoil (2 parts, and sand (1 part) was placed to a depth of 8 in. or more in each tank. Each container was filled to within 6 in. of the top with either dechlorinated tap water or spring water.

10. The following plants were used in the tests:

Plant	Source
Water hyacinth (*Eichhornia crassipes*)	Local, Florida
Alligator weed (*Alternanthera philoxeroides*)	Louisiana, Florida
Elodea (*Elodea Canadensis*)	Local, Florida
Hydrilla (*Hydrilla verticillata*)	Local, Florida
Eurasian water milfoil (*Myriphyllum spicatum*)	Local, Louisiana
Vallisneria (*Vallisneria americana*)	Florida
Cabomba (*Cabomba caroliniana*)	Florida, Louisiana
Water lettuce (*Pistia stratiotes*)	Louisiana
Southern naiad (*Najas guadelupensis*)	Florida
Coontail (*Ceratophyllum demersum*)	Louisiana

11. Plants were purchased or collected locally and in Florida. Many plants were furnished through the courtesy of Mr. William Thompson of the U. S. Army Engineer District, New Orleans, and Mr. Angus Ghoulson, Lake Seminole Reservoir, Chattahoochie, Florida.

2,4-D Solubilities in Elastomeric Matrices

12. The two formulations of 2,4-D chosen are insoluble in plastic materials such as poly (vinyl chloride), polyethylene, polypropylene, etc.; therefore, since solubility is essential to the functioning of a diffusion-dissolution mechanism, a number of elastomers were examined. Some degree of solubility is evident in the following common materials: chloroprene, butyl rubber, natural rubber (NRX), synthetic isoprene, styrene-butadiene (SBR), ethylene-propylene dimers (EPDM), acrylonitrile rubber of low acrylic content, and probably others. Based upon cost considerations, NRX, SBR, and EPDM were chosen for further study.

13. Simple weight gain (as a function of time) measurements made by curing the three candidate polymers and immersing them in the toxicant allowed the approximate determination of solubility limits. The following tabulation is illustrative:

		Cure Condition		Solubility	
Compound	Base	Time, min	Temp, °F	Butoxyethanol Ester (BEE), %	Dimethylamine (DMA), %
7ACE-A	EPDM	20	300	20.5	0.9
7ACE-B	EPDM	40	300	14.0	0.8
8ACE-A	NRX	20	300	36.2	1.0
8ACE-B	NRX	40	300	39.0	1.0
9ACE-A	SBR	90	300	11.8	0.5

14. Results were confirmed in later experiments as well as by observation during mill mix. Consequently, further effort with the dimethylamine was suspended. It is not to be construed that this form of 2,4-D cannot be used in slow-release systems. However, carrier additives would have to be found and this would constitute considerable effort thereby subtracting from the general goal. Likewise, SBR was discarded as a candidate base polymer due to the relatively low solubilities evidenced.

15. Essentially natural rubber is the best choice based on economy,

as well as high 2,4-D solvency, for the base polymer. Consequently, formulary work was concentrated on adding the ester (BEE) to NRX.

16. One anomaly does appear. It was expected that the "tighter" cure (longer cure time) "B" materials would be less of a solvent for 2,4-D. In the case of natural rubber, this is apparently not so. Perhaps long-term immersion results in some sort of reversion.

2,4-D Absorption by Carbon Black

17. Previous data indicated that carbon black as an additive would slow down loss rate. The higher the BEE absorption, the greater the diffusion path length, and thus a slower migration could be expected. In order to learn more about such absorption various carbon blacks were examined. Results are depicted in table C1:

Table C1

BEE Absorption by Carbon Black

Carbon Black Type	ASTM Code	Particle Size, μ	BEE Absorption (g BEE/10 g Carbon Black)
SAF	N110	20	8.2
SCF	N294	22	6.4
CF	N293	27	6.2
ISAF	N231	29	6.0
FEF	N550	70	6.0
ISAF	N220	29	5.8
ISAF	N219	29	5.2
HAF	N326	46	4.8
HAF	N330	45	3.3
SRF	N774	160	3.3
SRF	N770	128	3.2
MT	N990	462	2.8
FT	N880	256	2.5

18. In other words, SAF black will be the most effective in slowing down diffusion rate, and hence loss rate, and FT the least effective.

Rate adjustments are functions of both the type of carbon black and the amount used.

Product Design

19. The program envisioned five distinct types of slow-release products.

a. Floaters. Wherein the subject pellet floats on the surface of the water and releases 2,4-D as a surface film.

b. Sinkers. The pellets, which are slightly heavier than water, sink to the bottom of the watercourse. Here they lie on the bottom surface, or sink some depth into the bottom soil. 2,4-D is then released in the bottom mud, etc. These may be made in various densities if a selective bottom soil submergence depth is desired.

c. Suspenders. Such materials are shaped as ribbons or rods of 6- to 8-in. lengths. The rubber, per se, has a density of less than one. However, at one end of the major axis a dab of heavy paint, or a metal crimp, is used as a sinker. The material then rides with the light end at or just above the water surface and the heavy end down (see fig. C1). 2,4-D is thus released in the surface-to-6-in.-depth phytozone. In practice it was found convenient to use a heavier rubber at the lower end. Using a little heavier compound at the lower end, "bottom suspenders" that hover just off the bottom of the watercourse were created.

d. Bouquets. 2,4-D-loaded, floating, slow-release elastomers are extruded; chopped in strands of several feet in length; gathered in bundles; and weighted at one end. The result was a bouquetlike appearance with the union end resting on the watercourse bottom and the strands floating upward.

e. Time-capsule release. Here the floating pellets are encapsulated in a slowly exfoliating acrylic binder or a weighted gelatin capsule. The unit capsule sinks to the stream bottom, where it gradually dissolves releasing floaters or suspenders that move upward toward the water surface.

20. Fig. C1 illustrates these basic design concepts. The thrust, of course, is to release 2,4-D in the target phytozone.

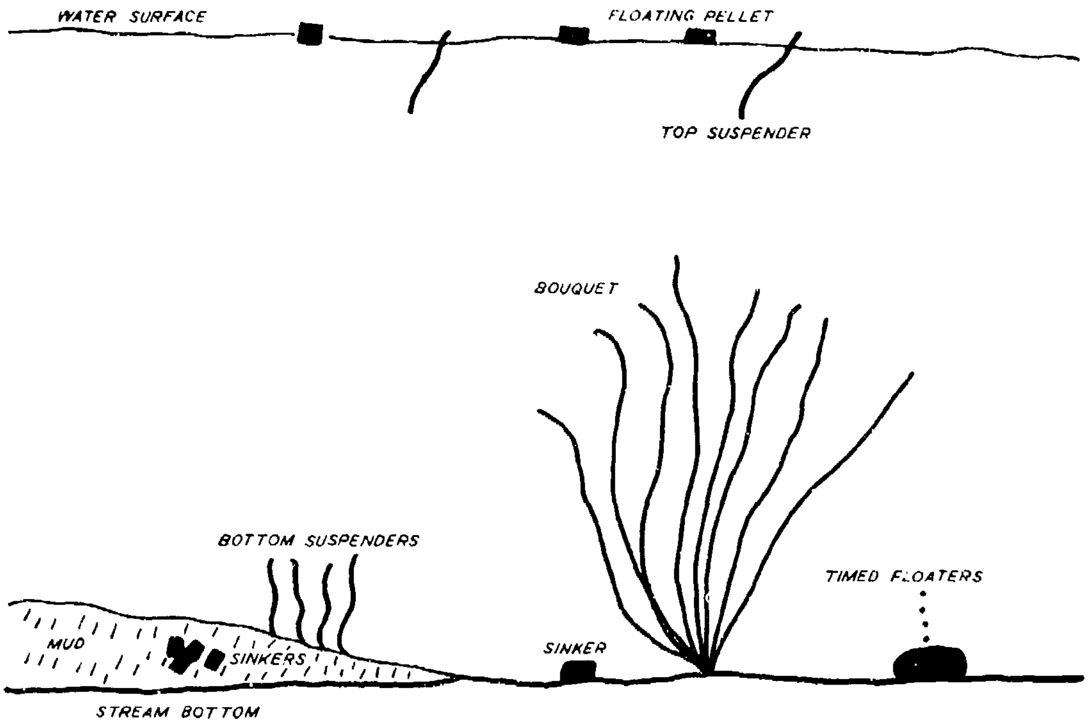

Fig. C1. Basic design concepts

21. The initial bouquets were made with latex thread dipped in a latex-2,4-D slurry. However, pickup was poor and only a few weight percent of the herbicide was coated. Later floating strands of EPDM- and NRX-based materials were extruded, bundled, and weighted for examination.

22. The release concepts described above were examined early in the program to determine processing methodology and cost. Floating and sinking pellets represent no factory problems and are easily produced at 40 to 45 cents per pound (not counting the cost of the 2,4-d, as loading levels are unknown) using standard equipment. A simple mix, extrusion, cure, and chopping system using small-scale equipment should allow 500 to 700 lb per hour production from one line. Suspenders are somewhat more elaborate, have a processing cost of 70 to 80 cents per pound (sans

2,4-D), and production on a similar line of 300 to 500 lb per hour.

23. Bouquets require an additional bundling and weighting step that will require somewhat more specialized equipment. However, in essence there is no particular difficulty involved in this process. It is estimated that bouquet costs would be 75 to 90 cents per pound (again without the cost of the active agent). The time-release capsules are easily made by hand; however, the actual mass production equipment needed and associated problems do not allow more than a crude estimate of 75 to 90 cents per pound, factory costs. Bagging and shipping expenses may add several more cents per pound in all cases. Estimates are based upon 25,000-lb production lots.

PART V: PHASE I FORMULATIONS

24. A number of compounds were prepared based upon 2,4-D solubility data and past experience. Variations in formulation were to examine the effects of the additives, cure system, etc. However, phase I compounds were generally aimed at assessing the validity of approach and determining if there is a diffusion-dissolution phenomenon and whether the release is efficacious. The possibility of decomposition or chemical reaction with compounding additives during the cure process was investigated. Actual matrix adjustments aimed at optimization occupied phase II work.

25. Mill-room operations were performed in-house and at Akron Rubber Development Laboratory, Inc. Materials were mixed on the mill, sheeted off, and either cured as 6- by 6- by 0.075-in. sheets or extruded as 1/8-in.-diam rods. Rods were cured under steam in an autoclave, cooled, and chopped into about 1/16-in. widths. Extrusions were not as smooth as desirable; however, it is not advisable to introduce silene, clay, etc., as smoothing agents, as interference with 2,4-D loss rates may occur.

26. Only superior candidates, judged by bioassay results, are listed below in the interest of saving expense and not boring the reader with many pages of irrelevant data. 2ACE, 3ACE, and 7ACE materials are nontoxic EPDM compounds for immersion studies and controls. 4ACE and 9ACE materials are SBR based and used as above. 8ACE compounds are nontoxic natural rubber for control and solubility evaluation purposes. 10ACE-E1, 11ACE-G, 11ACE-H, and 12ACE-6 dimethylamine (DMA), and though somewhat effective, have very short life times and low active agent concentration. All are overloaded and function by a leach mechanism. Their evaluation was discontinued when it became obvious that BEE/NRX and BEE/EPDM offered the best possibilities.

27. Likewise, all 12ACE series (7 compounds) were based upon an SBR matrix. Bioassay showed poor results due, undoubtedly, to low

concentrations, and this group was eliminated early in the program.

28. BEE was supplied without charge by AMCHEM Products, Inc. (Ambler, Pa.) and DMA, without charge, by the Diamond-Shamrock Co.

29. Table C2 presents those phase I compounds showing some degree of efficacy and serving as guidelines for phase II formulations:

Table C2

Phase I Compounds

Compound	Base Elastomer	BEE Toxicant, %	Type
10ACE-A	EPDM	4.5	Floater
10ACE-B	EPDM	6.6	Floater
10ACE-C	EPDM	7.9	Floater
10ACE-D	EPDM	12.5	Floater
10ACE-E	EPDM	15.9	Floater
10ACE-F	EPDM	14.5	Sinker
10ACE-G	EPDM	20.1	Sinker
10ACE-H	EPDM	11.6	Sinker
10ACE-I	EPDM	13.1	Floater
11ACE-A	NRX	4.4	Floater/suspender
11ACE-B	NRX	4.5	Floater/suspender
11ACE-C	NRX	8.6	Floater/suspender
11ACE-D	NRX	15.8	Floater/suspender
11ACE-E	NRX	22.0	Sinker
11ACE-F	NRX	8.0	Sinker
11ACE-H	NRX	4.3	Floater
11ACE-I	NRX	7.7	Sinker
11ACE-J	NRX	7.5	Sinker
11ACE-K	NRX	10.4	Sinker
11ACE-L	NRX	9.7	Sinker
14ACE-A	NRX	22.2	Floater/suspender

PART VI: PHASE II FORMULATIONS

30. Bioassay work, reported in later sections, indicated that the phase I materials shown in table C3 below, were superior. Consequently, phase II compounds were based upon these formulations with the general intent to increase toxicant concentration and loss rate.

Table C3

Effective Phase I Formulations

Compound	Base Elastomer	BEE Toxicant, %	Type	Effective Against
11ACE-E	NRX	21.8	Sinker	Hyacinth, elodea, and milfoil
11ACE-C	NRX	8.5	Floater	Hyacinth
11ACE-D	NRX	15.7	Floater	Hyacinth
11ACE-B	NRX	4.4	Floater	Hyacinth
10ACE-B	EPDM	6.5	Floater	Hyacinth
10ACE-C	EPDM	8.6	Floater	Hyacinth
10ACE-E	EPDM	15.8	Floater	Hyacinth
11ACE-F	NRX	7.2	Sinker	Hyacinth
11ACE-J	NRX	11.1	Sinker	Hyacinth
14ACE-A	NRX	22.2	Suspender	Hyacinth

31. Phase I results indicated from bioassay and other evaluations that:

a. The butoxyethanol ester is released and does destroy the water hyacinth.

b. Carbon black and various oils can be used to change loss rates.

c. BEE is the logical choice as the toxic agent.

d. Natural rubber is the best choice as the base matrix material.

e. A simple sulfur-tetramethylthiuram disulfide cure with zinc oxide is appropriate.

32. The next step was to optimize a natural rubber, BEE compound, to achieve an appropriate loss rate with the maximum amount of herbicide available for release.

33. A number of test formulations were made: floating, suspending, and sinking. The best material to date is 15ACE-B (a modified 11ACE-E) as determined from the following criteria:

a. Economy of materials
b. Efficacious loss rate
c. Easy processibility
d. Maximum BEE content

More "exotic" forms of natural rubber were used to achieve the proper matrix (i.e., highest possible BEE solubility limit). RSS #4* would hold, in solution equilibrium, about 35%. However, extrusions were poor with uneven dimensions, some volatilization occurred during cure, and the extruded rod required special handling due to extensive tackiness. Consequently, accelerated partially precured natural rubber that eliminated these difficulties was selected. The final formulation of 15ACE-B (sinker) is given below.

	Parts by Weight	Cost/pound	Composition %
PA-80†	75.0	$0.405	44.6
SMR-5††	25.0	0.320	14.9
Zinc oxide	1.0	0.820	0.6
Stearic acid	0.5	0.550	0.3
Santocure CBTS	2.0	0.760	1.2
TMTDS	1.0	1.900	0.6
Sulfur	0.5	0.850	0.3
BEE	63.0	0.610	37.5

† PA-80 is a crudely coagulated, pale, crepe-type natural rubber with about an 80% precure.

†† SMR-5 is a refined, rib-smoked sheet with castor oil added as a lubricant.

34. Materials cost of 15ACE-B appears to be in the $0.46-0.49 per

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* Rib-smoked sheet, grade 4 (about 18 cents per pound).

pound range. Processing costs are estimated to be $0.20 per pound, and factory bagging, storing, and handling $0.10 per pound. A total cost of $0.80 per pound in 10,000+ pound quantities is indicated before profit. A selling price of $1.30 to $1.50 per pound is a reasonable guess.

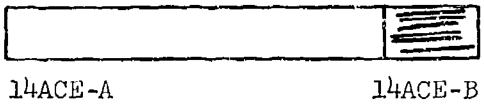
35. Early biological test results indicated that 15ACE-B is highly efficacious and that it may be desirable to slow down the release rate.

36. Optimum cure in air has been established as 270 F for 15 min. This is rapid enough to permit continuous cure by conventional methods of continuously extruding stock.

37. A good phase II floater, 14ACE-A, has likewise been formulated of the following recipe:

	phr
PA-80	75.0
SMR-5	25.0
BEE	30.0
Zinc oxide	1.0
CBTS	2.0
Stearic acid	0.5
TMTDS	1.0
Sulfur	0.5

38. An example of one suspender 14ACE-A/B, composed of two separate compounds molded together, is indicated below.



Property	Ingredient	Parts by Weight 14ACE-A	Parts by Weight 14ACE-B
Base elastomer	PA-80	75.0	75.0
Base elastomer	SMR-5	25.0	25.0
Active agent	BEE	30.0	30.0
Filler	AnO	1.0	60.0
Accelerator	CBTS	2.0	2.0
Processing aid	Stearic acid	0.5	0.5
Accelerator	TMTDS	1.0	1.0
Curative	Sulfur	0.5	0.5

39. Phase II formulations with NRX base are shown in table C4.

Table C4

Phase II Formulations (NRX Base), Sinker Type

Compound	BEE, %	Cure Conditions Temp, °F	Cure Conditions Time, min
15ACE-B(L)	37.5	270	15
15ACE-B(H)	37.5	300	30
16ACE-A	37.5	300	30
17ACE-B	37.5	290	30
17ACE-C	32.4	290	30
18ACE-B	33.5	290	30
18ACE-D	39.1	290	30
18ACE-E	44.7	290	30
18ACE-F	27.[illegible]	290	30
18ACE-G	32.3	290	30
18ACE-H	25.6	290	30

40. A number of formulations were prepared in which pellets of the floating compound 11ACE-D were encapsulated in Carboset.* These candidate materials were evaluated in water of 7.5 and 8.5 pH. Formulations are shown in table C5.

41. Results for superior formulations are shown in table C6. Those showing no release or fast release are omitted.

42. It is concluded that Carboset 525 provides the more rapid release and Carboset 526 the slower release. Likewise clay retards

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* Trademark, B. F. Goodrich Chemical Co. Cleveland, Ohio.

Table C5

Time-Release Formulations

Ingredient	A	B	C	D	E	F	G	H	J	K	L	M	N	O	P	Q	R	S
								Code 2OAC-										
Carboset 514	25	25	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Carboset 515	--	--	5	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Carboset 525	--	--	25	25	25	25	25	25	25	--	--	--	--	--	--	--	--	--
								Code 2OACE-Masters										
Water	75	75	--	75	75	--	--	--	--	50	--	--	--	--	--	75	--	--
Ethanol	--	--	75	--	--	75	75	75	75	25	75	75	75	75	75	--	75	75
Ammonia	5	5	5	10	10	5	5	5	5	5	5	5	5	5	5	5	5	5
Curative	2	2	2	--	2	--	1	1	2	--	1	1	1	2	--	--	1	1
Clay	25	50	--	--	--	--	--	50	50	--	--	25	50	50	25	--	--	25
Carboset [illegible]6	--	--	--	--	--	--	--	--	--	25	25	25	25	25	25	--	--	--
[illegible]	25	5	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Carboset 531	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	25	25	25

* Clay (bentonite) is used to increase the specific gravity of the mix above that of water.

Table C6

Time Capsule Evaluation

Compound 2OACE-	Time to Release, hr							
	Pellet Release, pH 7.5				Pellet Release, pH 8.5			
	25%	50%	75%	100%	25%	50%	75%	100%
A	2	8	12	18	2	7	10	17
B	3	8	13	18	2	6	11	16
E	2	5	9	15	1	3	7	14
F	6	12	17	24	4	10	15	20
H	2	5	9	15	1	4	9	14
J	2	3	4	5	0.5	0.8	1	2
O	--	--	--	--	40	48	60	72
[illegible]	8	12	30	48	4	8	24	36

release rate. For short-term (under 1 day) release a typical formulation would be:

Carboset 525	25 parts
Ethanol	75 parts
Ammonia	2 parts
Clay	(q.s. to increase gravity to 1.1)
Pellets	Under 50% total weight
Curative	None

For 1-week release a typical formulation would be:

Carboset 526	25 parts
Water	75 parts
Ammonia	1 part
Clay	20-40 parts
Pellets	Under 50% total weight
Curative	0.1 to 1 part

43. The pH variation, between 7.5 and 8.5, does not materially affect release rates of the compositions tested.

PART VII: BIOASSAY AND TEST PROCEDURES: WATER HYACINTH

44. Water hyacinth evaluations were performed in 5-gal containers. Three days after the containers were filled with water, a number of plants were added to each container and a 1-week stabilization period was allowed. Herbicidal formulations were then added in measured amounts. In indoor testing, water temperature was maintained at 78 to 82 F. Relative humidity was in the 90 to 98 range. Standard growth lights were used for illumination and a 14-hr-on, 10-hr-off cycle was established. Fertilizer in the amount of 25 g was added to each container. Results were recorded on a 0-to-100 range with "0" indicating a decayed, disintegrating plant that had sunk to the bottom, and "100" indicating a healthy plant with all upper leaves, etc., green. A "50" rating would show that 50% of the plant was dead or dying as indicated by leaf color and so on. Observations were admittedly subjective.

45. Outdoor tests, established in June 1970, were performed at the Norton test site, under normal climatic conditions. Daytime temperatures (°F) were generally in the middle 80's dropping to the lower 70's at night. Humidity varied from 60% to near 100% during June-July-August-September.

PART VIII: PHASE I EVALUATION

Water Hyacinth

46. Results of the indoor water hyacinth tests are shown in table C7.

Table C7

Water Hyacinth Indoor Tests

Compound	Dose, g	BEE, %	Type	Destruction, % Evaluation by Weeks Wk1	Wk2	Wk3	Wk4	Wk5	Wk6	Wk7
11ACE-E	1	21.8	Sinker	15	20	38	55	90	100	--
11ACE-E	0.5	21.8	Sinker	15	20	30	45	75	100	--
11ACE-E	0.1	21.8	Sinker	5	8	12	18	30	45	70
14ACE-A	5	22.2	Suspender	18	65	100	--	--	--	--
14ACE-A	1	22.2	Suspender	5	12	15	20	35	40	48
14ACE-A	0.5	22.2	Suspender	2	5	10	12	20	30	40
14ACE-B	2	18.0	Sinker	2	22	55	80	100	--	--
15ACE-B(L)	5	37.5	Sinker	10	18	50	70	100	--	--
15ACE-B(L)	2	37.5	Sinker	3	22	40	65	75	100	--
15ACE-B(L)	1	37.5	Sinker	2	5	10	12	18	25	55
15ACE-B(L)	0.5	37.5	Sinker	2	5	8	15	20	50	100
15ACE-B(L)	0.1	37.5	Sinker	0	2	5	10	15	30	65
15ACE-B(L)	0.05	37.5	Sinker	0	0	3	5	12	22	65
15ACE-B(H)	5	37.5	Sinker	5	10	18	55	90	100	--
15ACE-B(H)	1	37.5	Sinker	2	8	15	20	70	90	100
15ACE-B(H)	0.5	37.5	Sinker	0	2	5	7	25	85	95
17ACE-B	1	37.3	Sinker	5	20	30	40	45	70	100
17ACE-B	0.5	37.3	Sinker	0	3	5	10	20	50	70
17ACE-C	2	32.4	Sinker	2	12	15	10	10	15	20
18ACE-B	2	33.5	Sinker	5	15	65	80	100	--	--
18ACE-D	5	39.1	Sinker	5	15	65	100	--	--	--
18ACE-D	1	39.1	Sinker	2	15	35	40	60	90	100
18ACE-D	0.05	39.1	Sinker	5	15	25	35	75	90	100
18ACE-D	0.1	39.1	Sinker	2	5	5	5	5	10	15
18ACE-E	5	44.7	Sinker	2	10	75	100	--	--	--
18ACE-E	1	44.7	Sinker	2	5	5	5	--	--	--
18ACE-F	5	27.5	Sinker	2	15	80	100	--	--	--
18ACE-F	0.5	27.5	Sinker	2	5	55	100	--	--	--
18ACE-F	0.1	27.5	Sinker	2	2	2	2	--	--	--
18ACE-H	5	26.5	Sinker	2	15	75	100	--	--	--
18ACE-H	1	25.6	Sinker	2	5	5	5	10	--	--

47. A number of controls were run simultaneously with each group of evaluations. In general, indoor hyacinth controls showed 5% to 10% destruction over an 8-week evaluation period. Outdoor controls showed a 0% to 2% destruction. The use of nontoxic rubber at 10, 5, and 1 g per container showed no departure from natural control plant destruction. Insertion of 0.01 and 0.005 cc of 90% technical BEE gave a plant loss of: (average of 4, outdoor tests only)

Week 1 - 2%
Week 2 - 5%
Week 3 - 7%
Week 4 - 15%

48. It is concluded from the data above that compounds 11ACE-E, 15ACE-B(L), 18ACE-B, and 18ACE-F are superior.

49. The 18ACE series uses carbon black and phenolic "microballoons" as a means of regulating loss rates. In general, the higher black content, or the more structured (finer particle size) black, the slower the BEE release and hence the slower plant kill.

50. Various phase II plants used in the indoor tests were removed to outdoor containers to assess the degree of permanence of the observed deterioration. Water in the outdoor containers was toxic free. Recovery of these plants is rated in table C8.

51. It is believed that once a plant exhibits 90% or more destruction it does not recover; at 75% destruction there is stasis with, at most, a very slow regrowth. One group of plants removed at 75% to 85% destruction and observed for 10 weeks showed no new observable above-water growth.

52. It is known from instrumental data that initial release shows a rise to a peak and then a rapid decline to a continuous loss rate. It is believed, based on similar data from antifoulant and insecticide release, that the initial rise occurs during the first few days as the inevitable surface film of soapstone, dust, dirt, sulfur, bloom, etc., is washed away freeing an increasing amount of surface to water contact.

Table C8

Water Hyacinth Recovery

Compound	Rating by Weeks*					
	Wk0	Wk1	Wk2	Wk3	Wk4	Wk5
15ACE-B(L)	0	0	0	0	0	0
15ACE-B(L)	0	0	0	0	0	0
15ACE-B(L)	2	5	3	0	0	0
15ACE-B(L)	25	5	7	8	5	6
15ACE-B(H)	0	0	0	0	0	0
15ACE-B(H)	10	5	5	0	0	0
15ACE-B(L)	2	3	0	0	0	0
15ACE-D	0	0	0	0	0	0

* Rating at time of removal. 0 indicates plant had sunk, higher numbers indicate the amount (estimate) of "green" remaining on the plant at the time of removal from the treatment container.

Also the facial pore structure of the specimen in question, although it contains no higher toxicant concentration than the total sample, the molecules are more available and are lost by both diffusion-dissolution and simple leaching. As this area rapidly depletes, the loss curve declines until the diffusion rate is reached. Consequently, an experiment was devised wherein the sample pellets were kept in water (with hyacinths) for 1 week and 2 weeks, respectively. After this exposure period the pellets were removed to outdoor containers and exposed to new hyacinths. Outdoor results are given in table C9.

53. After removal of the test pellets from the indoor tests the plants continued to deteriorate from the 2,4-D concentration in the water. This is illustrated in table C10.

54. Five outdoor test pools completely covered with water hyacinths were treated with various compounds with results as tabulated

Table C9

Water Hyacinth Outdoor Tests

Compound	Pellet Presoak Period, weeks	Dose, g	Destruction, % Wk1	Wk2	Wk3	Wk4	Wk5
14ACE-B	1	2	7	15	15	17	55
15ACE-B(L)	1	2	5	23	45	70	100
17ACE-C	1	2	4	25	50	55	95
18ACE-B	1	2	3	32	40	43	60
14ACE-B	2	2	2	4	5	10	15
14ACE-B(L)	2	2	2	3	38	60	85
17ACE-C	2	2	2	2	15	18	25

Table C10

Water Hyacinth Indoor Tests After Removal of Pellets

Compound	Exposure Period, weeks, to 2-g Dosage	Destruction, % Wk1	Wk2	Wk3	Wk4	Wk5	Wk6
14ACE-B	1	2	23	45	60	80	100
15ACE-B	1	2	24	30	45	75	95
17ACE-C	1	2	14	14	11	15	18
18ACE-B	1	2	16	21	36	45	65
14ACE-B	2	2	18	40	53	75	100
15ACE-B	2	2	20	30	56	90	100
17ACE-C	2	2	10	10	10	10	15
18ACE-B	2	5	19	50	85	100	--

below. Pools 3 and 10 were hyacinth controls and showed no deterioration during the test period. Pools 12 and 13 showed copious blooming; pool 6 had a few blooms; and pool 11 had no blooms. Control pools were in continuous bloom.

Pool No.	Water Vol, gal	Dose ppm*	Compound	Type	Days (Destruction, %) E.R.**	10	25	50	80	99
6	1468	20	10ACE-D(T)†	Floater	7	10	--	--	--	-
11	752	20	14ACE-A	Suspender	2	6	12	16	22	28
12	752	20	15ACE-B	Sinker	18	--	--	--	--	--
13	752	50	11ACE-D	Floater	5	8	--	--	--	--

* Based on weight of pellet and not on weight of active ingredient.

** E.R. = epinastic response.

† 10ACE-D was enclosed in an 18-hr time release capsule similar to formulation 20ACE-A.

55. The suspenders became enmeshed in the hyacinth root system due to wind-driven currents, and it is believed that the close proximity of the ribbon to the plant created the dramatic effect shown. Both sinkers and surface floaters appeared to be inadequate from the standpoint of a rapid kill. Instrumental analysis of the BEE loss rate, from 14ACE-A, as reported in a later section, indicated such loss to be in the same order as that for sinkers and floaters. Hence, the actual intoxication of the phytozone appeared to provide greater efficacy. Observation of sinking pellets showed little or no settlement into bottom mud, at least in static pool tests. Floaters release toxicant in such a fashion (molecules, not droplets) as to create a surface film and, apparently, much of the active agent remains at the water surface. Consequently, suspenders, which release from the surface down to 6.5-in. depths have been postulated to be more effective, and pool tests seem to bear this out.

Elodea

56. Elodea was procured locally and propagated in an 8-ft-diam

vinyl pool. Tests were conducted in 1-gal wide-mouth jars with plants potted, three plants per jar, and completely submerged. All formulations were tested. Table C11 illustrates results from superior materials only. Spring water at pH 7.0 was used. Rich organic soil was used in potting.

Table C11

Phase I Elodea Evaluation

			Destruction, %						
Compound	Dose, g	Type	Wk1	Wk2	Wk3	Wk4	Wk5	Wk6	Wk7
10ACE-B	0.5	Floater	2	5	15	25	45	60	70
10ACE-G	0.5	Sinker	0	8	18	35	55	75	100
10ACE-G	1.0	Sinker	5	10	18	45	65	80	100
10ACE-H	1.0	Sinker	5	10	20	38	50	70	100
11ACE-D	1.0	Floater	10	50	80	85	100	--	--
11ACE-E	1.0	Sinker	80	100	--	--	--	--	--
11ACE-E	0.5	Sinker	2	5	20	60	75	95	100
11ACE-E	0.1	Sinker	0	2	2	2	2	--	--
14ACE-A	1.0	Suspender	0	2	2	5	15	25	40
15ACE-B(H)	5.0	Sinker	2	2	50	95	100	--	--
15ACE-B(H)	1.0	Sinker	2	2	2	55	100	--	--
15ACE-B(H)	0.5	Sinker	2	2	2	2	50	60	60
15ACE-B(H)	0.1	Sinker	2	2	2	2	50	50	50
16ACE-A	1.0	Sinker	2	2	2	95	100	--	--
16ACE-A	0.5	Sinker	2	2	2	40	50	50	50
16ACE-A	0.1	Sinker	2	2	2	20	35	40	40
17ACE-B	1.0	Sinker	2	2	85	100	--	--	--
17ACE-B	0.5	Sinker	2	2	60	100	--	--	--
17ACE-B	0.1	Sinker	2	2	50	80	75	75	80
18ACE-B	1.0	Sinker	2	5	70	80	80	90	90
18ACE-H	0.5	Sinker	2	2	90	90	100	--	--
18ACE-H	0.1	Sinker	2	2	15	20	20	25	25

57. It was observed that with lower dosages of 11ACE-D, 11ACE-E, and 17ACE-B that, whereas the plant stem darkened and lost all of its foliage, new green shoots emerged.

58. Eighteen control jars were run simultaneously. Of this number, at the end of the 7-week test period, 13 controls had less than 5% deterioration, two had 15%, one 30%, one 35%, and one 50%.

59. Elodea control with formulations prepared to date appears difficult. At this stage of the developmental program only 11ACE-E, 17ACE-B, 15ACE-B(H), and 18ACE-B appear to be effective. BEE is, of course, not as effective as other herbicides for elodea control, and it may well be that the incorporation of more adequate toxicants into slow-release matrices should be considered.

60. In outdoor pool tests, tank 1 was treated with 20 ppm of 18ACE-B and tank 2 was used as a control. A thick biomass was present at time 0 in each pool. The nontreated pool showed little loss, many and continuous blooms, with most plants rooting in the 6-in. bottom. In contrast, the treated pool showed an increasing loss of biomass with continual plant deterioration, no blooming, and little or no rooting. In 28 days the number of plants decreased at least 50%. Fifty-four days after treatment, the elodea was estimated to have decreased to 10% of its former mass. The pool bottom was visible on most areas. Plants still alive exhibited a black-brown coloration and little, if any, leaves save for areas of new budding.

Eurasian Water Milfoil

61. Water milfoil tests, shown in table C12, were performed in duplicate or triplicate with three plants potted per jar. Spring water of pH 7.0 was used in the 1-gal test containers. Milfoil propagation was poor under the laboratory conditions, and adequate numbers of plants were not available for satistically valid experiments. Results presented below are averages of two evaluations only. All tests were performed indoors under artificial lighting. 11ACE-E is believed to be the superior material in terms of milfoil control.

Table C12

Phase 1 Eurasian Water Milfoil Evaluation

Compound	Dose, g	Type	Destruction, % Wk1	Wk2	Wk3	Wk4	Wk5	Wk6	Wk7
10ACE-E	1.0	Floater	10	13	30	62	62	100	--
10ACE-E	0.5	Floater	7	15	20	40	50	40	30*
11ACE-D	1.0	Floater	2	40	55	55	55	55	60
11ACE-D	0.5	Floater	2	40	55	55	55	55	60
11ACE-D	0.1	Floater	2	25	50	55	55	55	60
11ACE-C	1.0	Floater	10	15	30	75	75	100	--
11ACE-E	1.0	Sinker	10	15	30	57	100	--	--
11ACE-E	0.5	Sinker	10	15	37	55	100	--	--
14ACE-A	1.0	Suspender	10	15	30	60	65	100	--
15ACE-B(L)	1.0	Sinker	10	15	35	40	52	100	--
15ACE-B(L)	0.5	Sinker	7	10	23	38	40	100	--
15ACE-B(L)	0.1	Sinker	10	15	40	53	53	100	--
15ACE-B(L)	0.05	Sinker	5	10	30	35	40	100	--
17ACE-B	1.0	Sinker	10	15	15	40	43	100	--
17ACE-B	0.5	Sinker	5	15	25	37	40	100	--
17ACE-B	0.1	Sinker	10	12	30	40	50	100	--
17ACE-C	1.0	Sinker	8	12	33	68	60	100	--
17ACE-C	0.5	Sinker	10	12	15	58	55	100	--
Control 1	0.0	--	5	5	5	5	5	5	5
Control 2	0.0	--	5	5	5	5	5	5	5
Control 3	0.0	--	10	10	10	10	10	5	5
Control 4	0.0	--	2	15	10	10	5	5	5
Control 5	0.0	--	2	2	2	2	2	2	2
Control 6	0.0	--	2	2	2	2	2	2	2
Control 7	0.0	--	2	2	2	2	2	2	--

* New shoots developed.

Alligator Weed

62. Alligator weed was evaluated both indoors and out, in 5-gal plastic containers. Five plants were rooted in each container using 4 in. of bottom soil. A few grams of fertilizer were added. Growth was profuse and rapid with tops 6 in. to 4 ft out of the water. What was

considered to be inadequate indoor lighting had no significant effect on the rapid growth of the plants. Table C13 illustrates test results of superior formulations. Again 11ACE-E is believed to be the superior material.

Table C13

Phase I Alligator Weed Evaluation

Compound	Dose, g	Type	Destruction, %						
			Wk1	Wk2	Wk3	Wk4	Wk5	Wk6	Wk7
11ACE-E	1.0	Sinker	2	17	80	95	100	--	--
11ACE-E	0.5	Sinker	2	11	30	30	30	--	--
11ACE-E	0.1	Sinker	2	10	10	10	10	20	20
14ACE-A	1.0	Suspender	2	10	10	10	10	10	10
15ACE-B(H)	1.5	Sinker	2	2	2	2	(I)*	(I)	(I)
15ACE-B(L)	1.0	Sinker	2	2	2	19	20	20	25
16ACE-A	5.0	Sinker	2	2	(I)	(I)	(I)	(I)	(I)
17ACE-B	1.0	Sinker	2	4	2	6	10	25	30
Control (avg of 7)			2	2	2	2	3	3	3

* I indicates indefinite or undetermined effect.

63. The 18ACE series is presently under test. Pool 7 containing alligator weed was treated with 20 ppm of 18ACE-B. After 4 weeks there was no noticeable effect.

isolated from the extraction procedure could then be simply dissolved in ethanol (which absorbs well below the 2,4-D chromopores).

66. A major concern in using this technique was in the possibility of ethylation. In checking for this no change was found in the absorption peaks even after allowing samples to remain at room temperature for a week. Either ethylation does not shift the peaks, or it does not occur to any significant amount.

67. In establishing this procedure the 2,4-D acid at 1×10^{-4} in ethanol was examined over a 205- to 400-µ range (Perkin-Elmer spectrophotometer). Two major bands were observed: 230 µ (16% transmittance) and 283 µ (61% transmittance). The latter band was used as it was better defined and relatively isolated.

68. A calibration of transmittance at 283 µ for various 2,4-D concentration levels was performed using a Beckman DU-2 spectrophotometer (slit width 0.065 mm for 100% reference transmittance through pure ethanol). The accompanying graph corresponded closely to Beer's Law.

69. After extraction of the water samples, 10 cc of ethanol was added to the extractant, solution occurred, and the transmittance was measured. By using the calibration curve a given transmittance was interpreted as weight.

70. Data have been obtained on a number of materials which indicate that the herbicide was released. However, the only useful data were those from the superior formulations. Table C14 illustrates the measured loss rates of 14ACE-B, the weighted end of the suspender.

71. The 2-g 14ACE-B sample had a surface area of about 13 cm^2. Its BEE loading was approximately 18% or 0.36 g in the subject sample. Total loss during the first 22 days was 15.90 mg leaving a residual of 0.344 g. Loss appeared to be steady at 0.55 mg or so per day. Hence, an absolute longevity of 0.344/0.00055 = 625 days (21 months) is possible, but not likely. It appears that dissolution at the interfacial area is controlling, and not diffusion within the rubber. The first process will give a relatively constant loss rate until internal

Table C14

14ACE-B Release Data

Day	2,4-D Loss,* mg
1	0.96
2	1.07
3	1.08
4	1.11
5	1.05
6	0.96
7	0.88
8	0.76
9	0.64
10	0.56
11	0.52
12	0.56
13	0.60
14	0.56
15	0.60
16	0.62
17	0.56
18	0.55
19	0.55
20	0.56
21	0.57
22	0.58

Note: Beckman DU-2 used.
Settings: PT selector 190-700 μ
Slit width: 0.064 mm
Sensitivity: 5
Zero suppression: Off
Screen bias: 4
* Computed as ester (2-g sample).

depletion is such that the molecular migration toward the surface becomes slower than the loss rate. When this will occur has yet to be discovered. Past experience with soluble toxicant diffusion through natural rubber would indicate that the constant loss rate observed will hold steady for 4 to 6 months, barring rubber degradation, and then drop rapidly to near complete depletion by the 12th month.

72. The loss rate data gathered for pertinent compounds are shown in table C15.

Table C15

Loss Rate Data from Superior-Candidate Slow-Release Herbicides

Compound	BEE* %	Type	Cure**	Black† phr	PT†† days	PL‡ mg/da	ET‡‡ days	EL§ mg/da	Longevity§§ months
14ACE-B	18.0	Suspender	U	0	4	1.11	10	0.56	21
15ACE-B(H)	37.5	Sinker	N	0	9	3.85	24	0.90	27
17ACE-B	37.3	Sinker	U	20	6	3.31	18	1.10	22
17ACE-C	32.4	Sinker	U	50	3	3.78	13	0.80	27
18ACE-A	0.0	Sinker	N	0	0	0.00	0	0.00	0
18ACE-B	33.5	Sinker	U+	0	3	3.67	20	2.50	9
18ACE-D	39.1	Sinker	U+	0	2	6.40	--	--	--
18ACE-E	44.7	Sinker	U	50	13	3.78	--	--	--
18ACE-H	25.6	Sinker	U	0	6	3.83	--	--	--

* BEE calculated as the ester.

** Cure conditions: U = undercured, U+ - very undercured, N = normal cure.

† Carbon black content in parts per hundred rubber. Black serves as a loss rate modulator.

†† PT = time to initial peak release.

‡ PL = loss per day of BEE (calculated as the ester) at the peak time for a 2-g sample (13 cm^2).

‡‡ ET = time to equilibrium and constant loss.

§ EL = loss per day of BEE for a 2-g (13-cm^2 surface area) sample at the equilibrium plateau.

§§ Longevity is estimated by use of the formula:

$$\frac{\%\ \text{BEE} \times 2\ \text{g}}{(\text{Loss/day in mg})\ (30\ \text{days/month})} = \text{lifetime}$$

73. This assumes a continuous loss at the equilibrium level until depletion which cannot occur. Eventually the diffusion rate will fall below the dissolution rate and the curve will drop rapidly to some threshold release below the phytotoxic level for the dosage used.

74. The phytozone treatment concept involves the release of the controlling agent in the living space of the plant, and presumes that the 2,4-D concentration is and will remain greatest in that area.

Floating pellets and top suspenders were created in order to more effectively release the agent in the water hyacinth phytozone. 2,4-D (BEE)* has a specific gravity of 1.225 at 30 C which might suggest that this material will rapidly sink to the bottom of the treatment water. Dr. Kerry Steward (USDA, Fort Lauderdale) and Dr. Edward Gangstad (Corps of Engineers, Washington) suggested that the vertical distribution of 2,4-D released in the upper water levels be checked.

75. A Plexiglas tube with 0.5-in.-thick walls, 6 ft high, and 4 in. in diameter was stopped with a Plexiglas plug at one end. Entry portals, 1/8 in. in diameter, were drilled at 6-in. intervals along its length. This unit was erected on a metal stand, and a large rubber band (1/2 in. wide) was placed over each orifice. By puncturing the self-sealing band, aliquots could be withdrawn from the center of each level. Washed floating pellets were placed in the water-filled tube (pH of 6.9 to 7.0) and allowed to stand overnight before any water samples were taken. After 24 hr, 20-ml aliquots were taken from each level and extracted for 2,4-D content. The extracts were analyzed on a Coleman 101 UV spectrophotometer for 2,4-D content. The procedure above was repeated periodically and the data plotted. The results obtained for sinkers and floaters are illustrated in fig. C2. Early data from the limited tests indicated the active agent becomes quickly dispersed with the greatest concentration in the topmost 50% of the water area. Oddly enough 2,4-D seems to concentrate 6 to 12 in. below the surface. Since these formulations release their active agent slowly, and thus from early indications of zone concentration the 2,4-D remains near the surface, both the floater and suspender may enjoy an advantage over other time-release preparations. In the case of the sinkers, the active agent is dispersed upward rather than remaining at the stream bottom level.

76. Release rate data were calculated on the most effective formulations by following the procedures described below. A known size and

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* (Base 89, Amchem Products Inc., Ambler, Pa.)

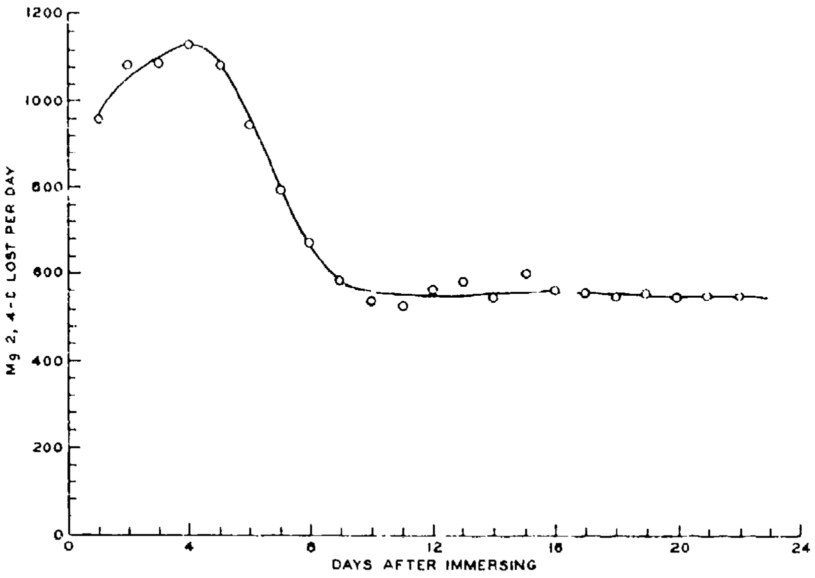

Fig. C2. Release rate of 14ACE-B (2,4-D BEE suspender pellets)

weight of specimen was suspended in 1000 ml of distilled water. The medium was changed every 24 hr by removing the sample from one container and immersing it in a container of fresh water to preclude the development of an equilibrium condition. The 2,4-D was isolated by extraction. Water samples were frozen to allow analysis at a later date. The following extraction procedure was used.

77. Graphs of 2,4-D losses are included as figs. C3 through C5. The percentages, by weight, of the butoxyethanol ester of 2,4-D for four carrier systems are shown below:

System	BEE (Base 89), % by Weight
11ACE-E	21.09
11ACE-C	12.34
15ACE-B(L)	37.50
14ACE-A/B suspenders	22.22
Bouquets	21.09

78. The half-lives of the formulations can be estimated from 1-g samples used in the loss rate studies:

System	Estimated Half-Life, days
11ACE-E	50
15ACE-B(L)	90
14ACE-A/B suspenders	265

The half-lives above can be varied by the use of additives or by the alteration of surface area (fig. C6). Fig. C7 shows the vertical distribution under static conditions of BEE as a function of time.

79. The dosage rates needed to control regrowth and/or existing growth are not yet known. The current practice of using 1-2 lb of the free acid equivalent per acre probably does not apply to the rubber carrier systems. For example, consider the suspenders. This compound contains approximately 22%, by weight, of the buxtoxyethanol ester of 2,4-D (which 79% of the 22% is the equivalent free acid). Using 17.3% (percent, by weight, of the free acid) of 40 lb rubber/acre yields 6.921 lb/acre free acid which would be equally dispersed over a life of perhaps 400 days, and thus the daily average would be quite small.

80. In the Plexiglas test chamber the water column was held static in so far as possible. Each orifice was closed by an encircling tight rubber ring. Aliquots were withdrawn by hypodermic puncturing of the ring. The rubber was self sealing so that no leakage occurred after the needle was withdrawn.

81. Total 2,4-D analysis (as the ester) from a 20-cc aliquot of the compound 11ACE-E, sinker (30 g), is as follows:

	Total 2,4-D Analysis, mg		
Water Depth	11 days	18 days	21 days
1.0 in.	0.90	2.63	1.65
0.5 ft	0.99	3.04	--
1.0 ft	3.04	3.65	1.59
1.5 ft	2.38	3.25	--
2.0 ft	3.04	1.30	--
2.5 ft	2.69	1.14	1.75
3.0 ft	0.74	1.51	--
3.5 ft	0.33	1.39	--
4.0 ft	1.01	1.78	1.35
4.5 ft	1.42	1.48	--

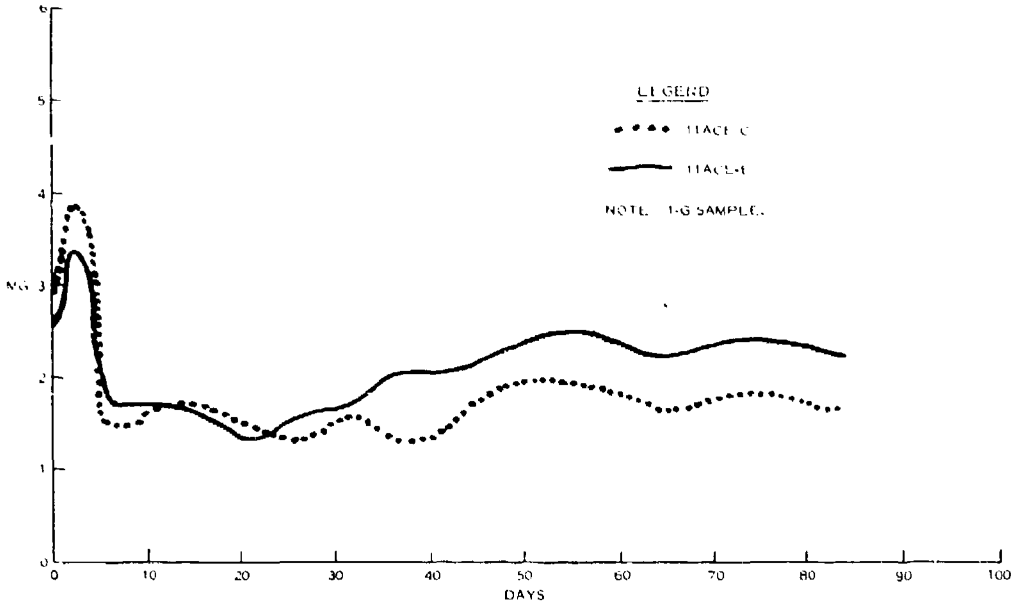

Fig. C3. 2,4-D release rates for 11ACE-C and -E systems

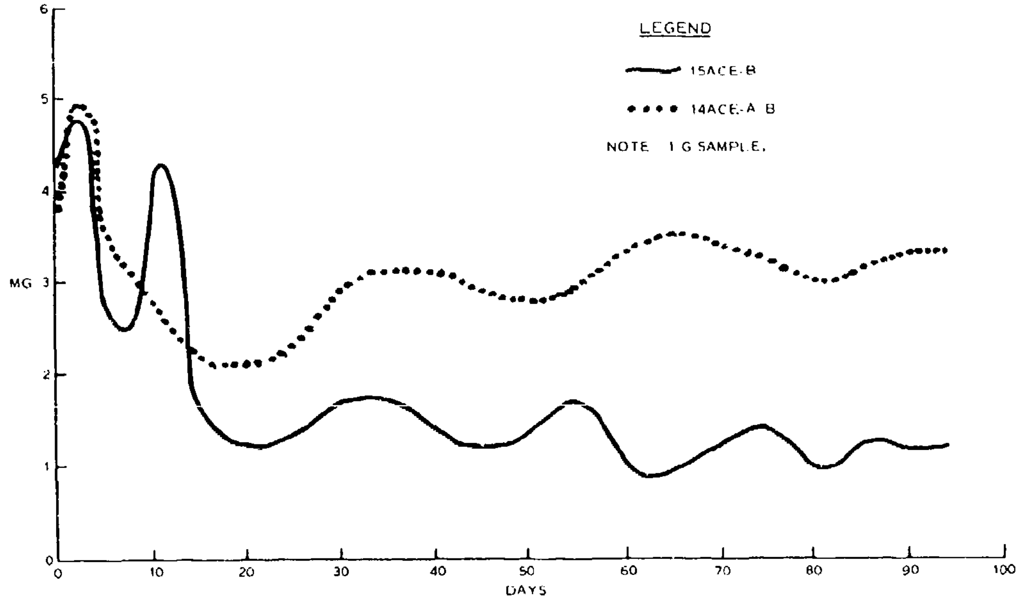

Fig. C4. 2,4-D release rates for 14ACE-A/B and 15ACE-B systems

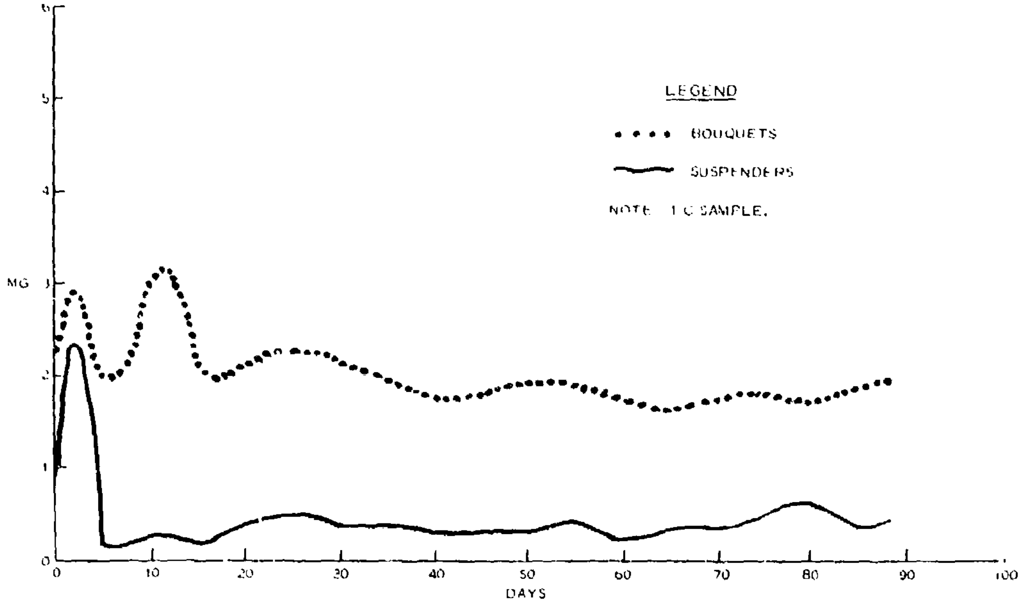

Fig. C5. 2,4-D release rates for bouquets and suspenders

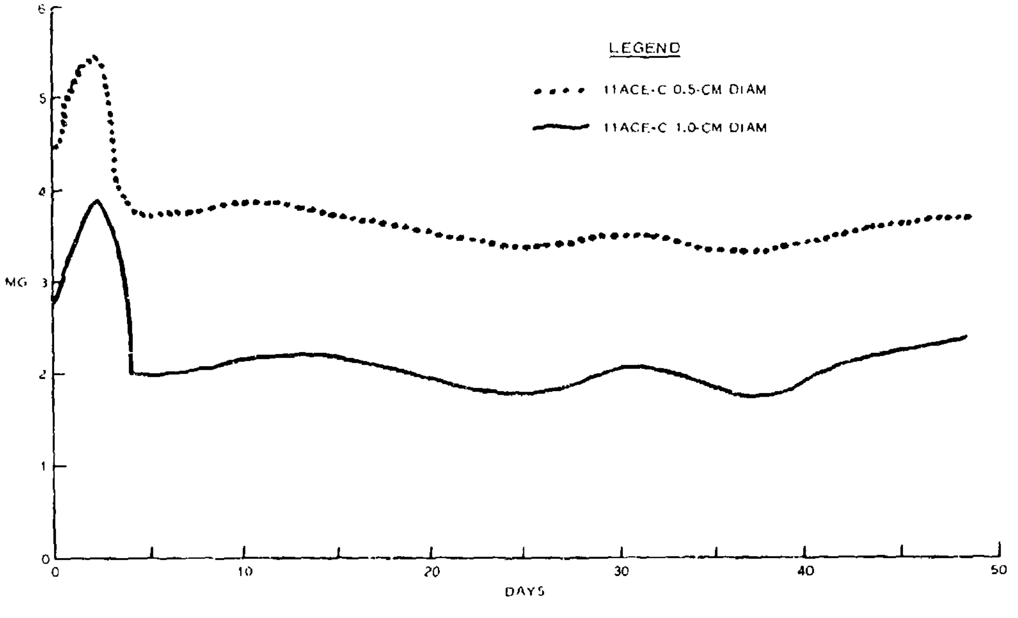

Fig. C6. 2,4-D release rates for 11ACE-C,
0.5- and 1.0-cm-diam surface areas

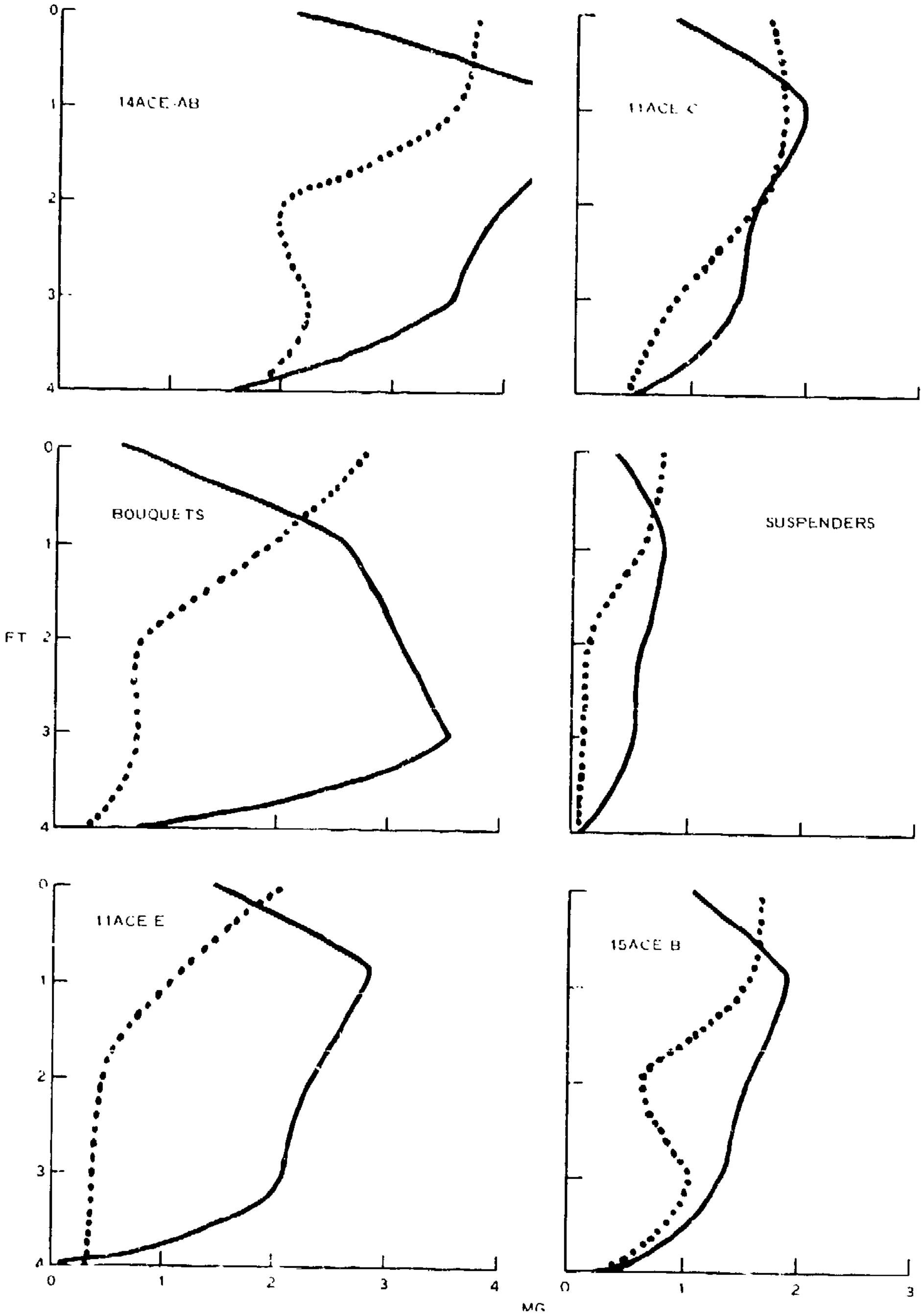

Fig. C7. Vertical distribution of BEE

82. The total released appeared to peak at 18 days with degradation being as great or greater than release after this time. After several weeks of sinkers releasing 2,4-D at the chamber bottom the dispersion appeared to be fairly uniform. Prior to equilibrium, 2,4-D seemed to rise rapidly, first saturating the surface layers and then gradually extending downward.

83. A 30-g sinker of 11ACE-E contains 6.6 g of BEE. The total water volume in the test chamber was 34×10^3 cc.

84. Total release at the maximum point was 21.17 mg in 200 cc, or 3.6 g in the total column. 11ACE-E appeared to release the herbicide very rapidly during the first few weeks. This may well account for the promising toxic action observed with several aquatic weeds. It is also noted that this material is the manufactured formulation prepared in quantity as a coarse powder. Release is much faster than with the larger pellets.

85. Total 2,4-D analysis (as the ester) from a 20-cc aliquot of the compound 11ACE-C, floater (30 g), is as follows:

	Total 2,4-D Analysis, mg		
Water Depth	2 days	9 days	11 days
1.0 in.	0.169	--	0.63
0.5 ft	--	1.72	0.58
1.0 ft	2.130	--	0.74
1.5 ft	--	1.61	0.58
2.0 ft	--	--	--
2.5 ft	1.690	--	--
3.0 ft	--	0.49	--
3.5 ft	--	--	--
4.0 ft	0.096	--	--
4.5 ft	--	0.42	--

This test is still in progress; however, it does appear that herbicide released from floating pellets tends to remain in the upper layers with very slow downward diffusion.

86. Several other pertinent materials have been examined and the release rate per square centimeter per day on a given day after immersion is shown below:

		Release Rate (in mg*) per cm^2 per day on day				
Material	Type	1	5	10	14	31
14ACE-A	Suspender	0.40	0.02	0.03	0.02	--
18ACE-H	Sinker	0.60	0.10	0.07	0.03	--
13ACE-F	Sinker	0.70	0.10	0.07	--	0.02
11ACE-E	Floater	0.15	--	--	0.17	0.15
11ACE-C	Sinker	0.15	0.16	--	0.03	--
14ACE-A/B	Suspender	0.35	0.27	--	0.22	--
15ACE-B	Sinker	0.27	0.42	--	0.16	--
14ACE-B	Sinker	0.21	0.31	--	0.22	--

* Calculated as the ester. Multiply by 0.79 to compute the acid equivalent.

PART X: PHASE II EVALUATIONS

87. Phase II studies were initiated indoors under growth lights. Initially, the work described previously was repeated but with more sophisticated pellets processed by factory equipment at Akron Rubber Development Laboratories. Tables C16, C17, and C18 are evaluations of alligator weed, elodea, and water milfoil, respectively, after treatment. Only 11ACE-E showed any short-term effects against alligator weed, and even then at pellet concentrations far above the practical. 11ACE-D, a floating pellet, does not appear to be nearly as effective as suspenders or sinkers against water milfoil.

Table C16

Phase II Alligator Weed Evaluation

Compound	% 2,4-D	Dose* g/gal	Type	% Mortality** Wk2	Wk4	Wk6
15ACE-B	37.6	0.1	Sinker	2	2	2
15ACE-B	37.6	0.5	Sinker	2	2	70
15ACE-B	37.6	1.5	Sinker	2	10	70
17ACE-C	32.6	0.1	Sinker	2	2	5
17ACE-C	32.6	0.5	Sinker	2	2	5
17ACE-C	32.6	1.5	Sinker	2	2	5
Control	0.0	0.0	--	2	2	2
11ACE-D	15.8	0.1	Floater	2	5	5
11ACE-D	15.8	0.5	Floater	2	25	40
11ACE-D	15.8	1.0	Floater	20	32	45
Control	0.0	0.0	--	5	5	15
11ACE-E	22.0	0.1	Sinker	8	12	15
11ACE-E	22.0	0.5	Sinker	30	30	65
11ACE-E	22.0	1.0	Sinker	95	100	100
14ACE-A	22.2	0.1	Suspender	1	2	2
14ACE-A	22.2	0.5	Suspender	1	2	2
14ACE-A	22.2	1.0	Suspender	10	10	5
Control	0.0	0.0	--	1	2	2
17ACE-B	37.3	1.0	Sinker	8	40	40
17ACE-C	32.4	1.0	Sinker	4	15	20
10ACE-E	15.9	1.0	Floater	2	2	4
Control	0.0	0.0	--	5	10	10
16ACE-D	39.1	1.0	Sinker	6	10	10
Control	0.0	0.0	Sinker	5	5	5
10ACE-E	15.9	0.5	Floater	5	5	5

* Grams of pellets.
** Average of two or more replicates.

Table C17

Phase II Elodea Evaluation

System	% 2,4-D	Dose g/gal	% Mortality Wk1	Wk2	Wk3	Wk4	Wk5	Wk6	Wk7
11ACE-D, floater	15.8	0.1	2	25	50	55	55	55	55
		0.5	2	55	55	55	55	55	60
		1.0	2	40	55	55	55	55	60
Controls (Avg of three)	0.0	0.0	2	4	4	4	4	5	8

Table C18

Phase II Water Milfoil Evaluation

Compound	% 2,4-D	Dose g/gal	Type	% Mortality Wk1	Wk2	Wk3	Wk4	Wk5	Wk6
11ACE-C	8.6	0.1	Floater	2	5	10	60	57	55
11ACE-C	8.6	0.5	Floater	2	2	2	10	50	80
11ACE-C	8.6	1.0	Floater	2	2	15	20	65	90
11ACE-D	15.8	0.1	Floater	10	30	25	--	--	--
11ACE-D	15.8	0.5	Floater	30	50	35	--	--	--
11ACE-D	15.8	1.0	Floater	50	80	85	97	100	100
11ACE-E	22.0	0.1	Sinker	2	2	2	12	11	13
11ACE-E	22.0	1.0	Sinker	2	2	25	25	90	100
15ACE-B	37.6	5.0	Sinker	2	50	95	100	100	100
15ACE-B	37.6	1.0	Sinker	2	2	55	95	100	100
15ACE-B	37.6	0.5	Sinker	2	3	3	50	48	--
15ACE-B	37.6	0.1	Sinker	2	2	2	50	45	--
16ACE-A	37.5	1.0	Sinker	2	2	95	94	100	100
16ACE-A	37.5	0.5	Sinker	2	2	40	50	--	--
16ACE-A	37.5	0.1	Sinker	2	2	20	50	--	--
17ACE-B	37.3	5.0	Sinker	2	2	95	100	100	--
17ACE-B	37.3	1.0	Sinker	2	2	95	95	92	--
17ACE-B	37.3	0.5	Sinker	2	2	80	75	70	--
17ACE-B	37.3	0.1	Sinker	2	2	2	2	2	--
17ACE-C	32.4	1.0	Sinker	2	2	20	50	--	--
17ACE-C	32.4	0.5	Sinker	2	2	20	18	--	--
17ACE-C	32.4	0.1	Sinker	2	2	15	14	--	--
Controls (3)	0.0	0.0	--	2	2	5	25	22	20
18ACE-B	33.5	1.0	Sinker	5	5	90	95	98	100
18ACE-B	33.5	0.5	Sinker	2	2	20	50	45	42
18ACE-B	33.5	0.1	Sinker	2	2	15	15	35	50
18ACE-D	39.1	1.0	Sinker	2	10	20	80	90	92
		0.5	Sinker	2	10	20	30	50	80
		0.1	Sinker	2	10	20	16	12	2

88. Outdoor pool tests were begun in May 1970. Results are shown in table C19.

Table C19

Outdoor Pool Tests

Pool No.	Plant	Compound	Dose ppmw	% Mortality Wk1	Wk2	Wk3	Wk4	Wk5	Wk6	Wk7
1	Elodea	18ACE-B	1	0	7	20	50	50	50	40
2	Elodea	0	0	0	0	0	0	0	0	0
3	Hyacinth	0	0	0	0	0	0	0	0	0
4	Alligator weed	0	0	0	0	0	0	0	0	0
5	Alligator weed	0	0	0	0	0	0	0	0	0
6	Hyacinth	10ACE-D	1	0	2	2	2	2	2	2
7	Alligator weed/elodea	18ACE-B	1	0	2	2	2	5	5	5
8	Hyacinth	14ACE-B	1	0	0	2	2	2	2	2
9	Elodea	0	0	2	2	2	2	5	5	5
10	Hyacinth	0	0	0	2	2	0	2	1	2
11	Hyacinth	14ACE-A	1	10	30	75	95	98	98	98
12	Hyacinth	15ACE-B	1	2	2	2	2	2	2	2
13	Hyacinth	11ACE-D	1	5	10	10	10	10	12	12

The dramatic comparison between pools 3 (control), 11 (suspender), 12 (sinker), and 13 (floater) illustrate the value of treating the phytozone. Suspenders release 2,4-D at approximately the water surface down to the 6.5-in. depth.

89. All pools received a second treatment after the initial round reported in table C19 with the following observations as shown in table C20. Compounds remained in the respective pools over the winter. Plant regeneration, 2,4-D water content, and continued efficacy of the formulations were checked in the spring and no regrowth was found.

90. The following data, based on experience and present work at Akron Rubber Development Laboratories, Inc., allows the presentation of the following estimates. Figures are based upon 10,000-lb lots with a constant 35% BEE active agent.

Table C20

Second Pool Treatment

Pool No.	Plant	Compound	Type	Dose ppmw	% Mortality Wk1	Wk2	Wk3	Wk4	Wk5
1	Elodea	11ACE-C	Bouquet*	1.2	2	2	2	2	2
2	Elodea	0	0	0.0	0	0	0	0	0
3	Hyacinth	11ACE-E	Sinker	1.0	5	5	15	20	32
4	Alligator weed	11ACE-C	Bouquet	1.2	2	2	2	5	12
5	Alligator weed	11ACE-E	Sinker	1.0	5	5	5	5	15
6	Hyacinth	11ACE-C	Bouquet	1.3	5	10	15	20	32
7	Alligator weed/elodea	14ACE-A	Suspender	1.0	2	2	2	2	8
8	Hyacinth	14ACE-A	Suspender	1.0	5	5	5	15	30
9	Hyacinth/elodea	11ACE-E	Sinker	1.0	5	5	8	12	24
10	Hyacinth	11ACE-C	Floater	1.0	5	5	5	5	35
11	Hyacinth	14ACE-A	Suspender	1.0	(100% mortality)				
12	Hyacinth	11ACE-E	Sinker	1.0	5	5	5	10	35
13	Hyacinth	11ACE-D	Floater	1.0	(30% mortality)				
14	Alligator/hyacinth	11ACE-C	Bouquet	1.3	5	5	5	5	40

* Each bouquet contains 6 strands, 1.5 ft in length.

91. Raw materials costs are as follows:

	per lb
Sinking pellet	$0.480
Floating pellet	0.495
Suspender	0.520
Time release	0.680
Bouquet	0.495

92. The following processing costs (per pound of stock) for each step have been estimated based on a factory cost of $8.00 per man-hour.

Step	Costs Sinker	Floater	Suspender	Time Release	Bouquet
1. Raw materials handling	$0.03	$0.03	$0.03	$0.05	$0.03
2. Mixing of materials	0.04	0.04	0.07	0.04	0.04
3. Distribution	0.01	0.01	0.01	0.01	0.01
4. Extrusion	0.01	0.01	--	0.01	0.02
5. Cure (preparation)	0.05	0.05	0.06	0.05	0.05
6. Cure (continuous)	0.01	0.01	0.02	0.01	0.01
7. Pelletizing	0.02	0.02	0.03	0.02	0.05
8. Binding	--	--	--	0.04	0.02

(Continued)

Step	Costs Sinker	 Floater	 Suspender	 Time Release	 Bouquet
9. Bagging	0.01	0.01	0.02	0.03	0.02
10. Storage and transportation	0.01	0.01	0.01	0.02	0.02
11. Factory materials	0.02	0.02	0.02	0.01	0.02
Total factory labor and overhead	$0.21	$0.21	$0.27	$0.29	$0.29
Raw materials	$0.48	$0.50	$0.52	$0.68	$0.50
General and administrative (5%)	$0.01	$0.01	$0.01	$0.01	$0.01
Mfg cost (per pound of bagged stock)	$0.70	$0.72	$0.80	$0.98	$0.80

93. Add to these figures, setup charges, profit, warehousing, and shipping, and an ultimate purchasing price of $1.30 to 1.50 per pound is envisioned.

94. Floating and sinking pellets are easily manufactured on equipment routinely available with any manufacturer of rubber goods. Essentially these materials can be mixed by mill or Banbury, extruded through a 4 to 60 hole (1/16-in.) die, into a soapstone/water emulsion, cured on a continuous line through an air oven (300 F for 3 to 6 min should be adequate using partially precured rubber), chopped, and bagged as a continuous semiautomatic process.

95. Bouquets are chopped in 3- to 6-ft lengths of extruded rod, rather than 1/8 in. or so for pellets; after chopping bouquets are placed in a clamp-binder machine that unites one end of 12 or more strands with a metal clamp.

96. Suspenders present much greater difficulty in that two uncured stocks must be mated together prior to cure. This can be done by a continuous press cure line with two stock feeds, but it is expensive. Whereas a whirling knife or horizontal knife chopper can be used with pellets, suspenders require precutting of 6-in. and 1-in. widths of the two stocks, and then trimming after cure.

97. Time release floaters, as envisioned, do not lend themselves to simple manufacturing processes. Carboset preparations can be cost dried from water or water/alcohol solutions; however, this is costly. Hot-melt preparations are feasible, but special equipment is needed. The manufacturing methodology will turn with the envisioned use. If the purpose of a time release capsule is to break foliage, this can be simply done by packaging the floating pellets in a large weighted gelatin capsule. This will release in a few minutes to a few hours. However, if a slow release of pellets is necessary over a few days to a few months period, the more difficult, and more expensive, encapsulation will be necessary.

98. PN2742-5, a compound of 10% BEE in a liquid SBR-type rubber, was used to treat water hyacinth. At 1 g/gal an 80% kill was observed by the third week in indoor tests; 100% kill was achieved in the fifth week. Lower dosages were not overly effective. Tests are continuing.

PART XI: MANUFACTURING ANALYSIS

99. A production line flow is being planned. Preliminary figures indicate the following rough manufacturing costs, excluding storage, shipping, overhead, and profit.

Compound	Type	100 lb	2000 lb	10,000 lb	100,000 lb
14ACE-A/B	Suspender	$5.00/lb	$3.50/lb	$2.50/lb	$1.50/lb
11ACE-C	Floater	$3.00/lb	$2.50/lb	$1.75/lb	$1.25/lb
11ACE-C	Bouquet	$3.50/lb	$2.75/lb	$2.00/lb	$1.35/lb
11ACE-E	Sinker	$3.00/lb	$2.25/lb	$1.60/lb	$1.10/lb

100. The following compounds have been manufactured on a pilot scale by the Akron Rubber Development Company. 11ACE-C bouquets have been sent to various interested collaborators. 11ACE-E has been prepared as several grades of rough powder. At 1 g/gal- and 0.2 g/gal-level, water hyacinth destruction was 80% by the third week (indoor bench tests).

Compound	Quantity, lb	Type
11ACE-C	100	Floater
11ACE-E	100	Sinker
14ACE-A/B	115	Suspender
11ACE-C	25	Bouquet

PART XII: PHASE II TIME-RELEASE CAPSULES

101. The Carboset family of acrylics were utilized as binders in the effort to formulate a variable time-release capsule. The addition of various clays to the Carbosets enhanced release time and adjusted the specific gravity. The addition of varying cure levels increased the lifetime of the capsule. The following compounds were formulated:

Ingredient	21ACE-A	21ACE-B	21ACE-C	21ACE-D
Carboset 514	50	40	40	40
Water	25	35	30	35
NH_4OH (28%)	5	5	5	5
Bentonite (clay)	18	18	25	--
Attaclay	--	--	--	18
Suspenders (active agent)	30	15	15	15
ZnO complex	2	2	--	2

	21ACE-E	21ACE-F	21ACE-G	21ACE-H	21ACE-I
Carboset 531	15	15	--	--	--
Carboset 526	--	--	15	15	10
Ethanol	60	60	45	45	50
NH_4OH (28%)	5	5	5	5	5
ZnO complex	2	2	2	2	2
Suspenders	15	15	15	15	15
Bentonite	18	--	33	--	33
Attaclay	--	18	--	33	--

	21ACE-J	21ACE-K	21ACE-L	21ACE-M
Carboset 526	20	30	30	30
NH_4OH (28%)	5	5	5	5
Ethanol	30	40	40	40
ZnO complex	5	5	2	1
Suspenders	15	15	15	15
Bentonite	40	20	20	20

(Continued)

Ingredient (cont'd)	21ACE-N	21ACE-O	21ACE-P	21ACE-Q
Carboset 526	10	20	20	20
NH_4OH (28%)	5	5	5	5
Ethanol	35	40	40	40

	21ACE-N	21ACE-O	21ACE-P	21ACE-Q
ZnO complex	5	5	2	1
Suspenders	20	20	20	25
Bentonite (clay)	40	30	20	20

The above-listed materials were poured into molds and baked at 150 F until dry. The solid time-release pellets were then placed in 1000-ml beakers containing water at pH's of 6.5 and 7.5, respectively.

102. Early indications from the tests established release rates for two of the encapsulated compounds under static water conditions:

21ACE-A	16-18 days
21ACE-C	30-32 days

The test results will not be directly applicable to field situations due to their static condition, but will serve as initial guidelines for further development.

103. The compounding of envelopes that dissolve in 1 to 60 days with specific gravities from 1.0 to 2.5 may have the following advantages:

a. Ease of dispersal.

b. Can be used as either a pretreatment or posttreatment.

c. Applied in slow growth months (winter) and released in the spring, thus better utilization of labor.

104. The slow release of aquatic herbicides from elastomeric matrices offers substantial promise as an economic means of controlling unwanted aquatic growth. Laboratory efficacy has demonstrated the feasibility of the method. The scope of the past program has encompassed only one form of 2,4-D which does not possess a high degree of

effectiveness against many aquatic weeds. Consequently, the program has been expanded to include those agents having high efficacy against the various plants in question. Furthermore, slow release, to achieve maximum economy, must act through the chronic phytotoxicity rather than the acute. Present conventional treatment utilizes massive dosing to rapidly destroy the pest--and requires repeat application within a few weeks or few months. In contrast, the continuous presence of a low level of phytotoxicity over months or years will, it is hypothesized, destroy the same growths. Probably of even greater importance, most plants are much more susceptible when seedlings or immature--and regrowth can be, it is believed, effectively prevented by persistent low dosage. That is, destruction or retardation through chronic effects will occur.

PART XIII: CHRONIC DOSE STUDIES

105. Briefly, it was the intent of the chronic dose study to apply a continuous low dose of a number of known in-use aquatic herbicides to major aquatic pest plants. Various chronic dosage rates were to be used against mature and immature plants. Exposure time was likewise to be varied ranging from two weeks to four months. Plants were to be continuously observed and effects recorded.

106. A number of 1-gal jars and 5-gal baskets were set up containing three or more mature plants. Two distinct experiments were under way (outdoors): (a) accumulative dose effects by adding a measured amount of herbicide each day; and (b) adding a daily herbicide dose, but with the water changed each day. In the latter case dose was held fairly constant.

107. Toxicant levels of 0.1 ppmw, 0.01 ppmw, and 0.001 ppmw were used. Also run in parallel were control plants (no dose) and 1 ppmw as a typical, though low, conventional dose rate.

108. The following evaluations were under way:

Herbicide	Plant
Dichlobenil	Elodea, naiad, milfoil
2,4-D butylester	Elodea, hyacinth, milfoil
Fenuron	Elodea
Silvex	Hyacinth, milfoil, alligator weed
2,4-D dimethylamine	Hyacinth
Fenac	Milfoil, vallisneria, alligator weed, naiad, cabomba
2,4-D butoxyethanol ester	Vallisneria, milfoil
2,4-D oleylamine	Hyacinth, milfoil
2,4-D acid	Hyacinth, alligator weed

109. It was also planned to initiate the following when herbicides were received:

Herbicide	Plants
Endothal acid	Elodea, milfoil, cabomba
Acrolein	Elodea
Endothal amine	Elodea, hyacinth
Diquat	Elodea, hyacinth, milfoil, naiad, water lettuce
Hydrothol	Elodea
Endothal (disodium)	Cabomba

110. Tests were initiated in June. However, further work on this study will not be reported on the subject contract as it has been terminated. All studies were performed in duplicate.

111. Tables C21, C22, and C23 show the initial results.

Table C21

Chronicity Study: Accumulated Dose

Plant	Agent	Dose ppmw	No. Days to % Plant Deterioration										
			5%	10%	20%	30%	40	50	60	70	80	90	100
Naiad	Fenac	1.0	2	4	4								
Naiad	Fenac	0.1	3										
Naiad	Fenac	0.01											
Naiad	Dichlobenil	1.0	3	4	5	5	5	6					
Naiad	Dichlobenil	0.1	6	6	6								
Naiad	Dichlobenil	0.01	6										
Elodea	Dichlobenil	1.0	2	3	3	3	4	5	5	5			
Elodea	Dichlobenil	0.1	3	3	5	6	6	6	6	6			
Elodea	Dichlobenil	0.01	4	5									
Elodea	Fenac	1.0	3										
Elodea	Fenac	0.1											
Elodea	Fenac	0.01											
Vallisneria	Fenac	1.0	2	2	2	3	3	4	4	4			
Vallisneria	Fenac	0.1	2	2	3	3	3						
Vallisneria	Fenac	0.01	5										
Vallisneria	BEE	1.0	4	5									
Vallisneria	BEE	0.1	5										
Vallisneria	BEE	0.01											
Milfoil	2,4-D butyl	1.0	1	2	2	3	4	4					
Milfoil	2,4-D butyl	0.1	1	2	2								
Milfoil	2,4-D butyl	0.01	5										
Milfoil	Fenac	1.0	1	2	3	4	4	4					
Milfoil	Fenac	0.1	1	2	2								
Milfoil	Fenac	0.01	4										
Milfoil	BEE	1.0	1	2	2	2	3	3	3	3			
Milfoil	BEE	0.1	2	3	3								
Milfoil	BEE	0.01	3										
Milfoil	2,4-D oleylamine	1.0	1	1	2	2	3	3	3	3			
Milfoil	2,4-D oleylamine	0.1	1	2	3	3	3						
Milfoil	2,4-D oleylamine	0.01	3	3									
Milfoil	Silvex	1.0	1	2	2	2	2	2	2	3	3	3	3
Milfoil	Silvex	0.1	1	2	2	2	2	3	3				
Milfoil	Silvex	0.01	2	3	3								
Cabomba	Fenac	1.0	3	3	3								
Cabomba	Fenac	0.1	3	4	5								
Cabomba	Fenac	0.01											

Table C22

Chronicity Study: Basket Tests

Experiment 1

Plant	Agent	Dose ppmw	Weekly Readings, % Deteriorated Wk1	Wk2	Wk3	Wk4
Hyacinth	2,4-D butyl	0.1	2	2	2	5
Hyacinth	Silvex	0.1	2	2	10	50
Hyacinth	2,4-D oleylamine	0.1	2	4	15	--

Table C23

Chronicity Study: Constant Toxicant Level

Experiment 2

Plant	Agent	Dose ppmw	No. Days to % Plant Deterioration 5%	10%	20%	30	40	50	60	70	80	90
Cabomba	Fenac	1.0	2	3	3	4	4					
Cabomba	Fenac	0.1	3	3	4							
Cabomba	Fenac	0.01	4									
Milfoil	2,4-D butyl	1.0	1	1	2	2	2	2	3	3	3	
Milfoil	2,4-D butyl	0.1	1	1	2	2	2	3	4	4	4	
Milfoil	2,4-D butyl	0.01	3	3	4	4	4					
Milfoil	Fenac	1.0	1	1	2	2	2	3	3			
Milfoil	Fenac	0.1	2	3	4	4						
Milfoil	Fenac	0.01	2	2								
Milfoil	2,4-D BEE	1.0	1	1	1	2	2	2	2	3	3	
Milfoil	2,4-D BEE	0.1	1	2	2	3						
Milfoil	2,4-D BEE	0.01										
Vallisneria	Fenac	1.0	2	2	2	3	3	4	4	4	4	
Vallisneria	Fenac	0.1	2	3	4	4	4					
Vallisneria	Fenac	0.01	5									
Elodea	Dichlobenil	1.0	2	2	3	3	4	4	5	5	5	
Elodea	Dichlobenil	0.1	4	4	5							
Elodea	Dichlobenil	0.01	3									
Elodea	2,4-D butyl	1.0	1	1	1	3	3	3				
Elodea	2,4-D butyl	0.1	1	3								
Elodea	2,4-D butyl	0.01										
Naiad	Dichlobenil	1.0	3	4	4	4	4	4	4	5	5	
Naiad	Dichlobenil	0.1	4	5	5							
Naiad	Dichlobenil	0.01	5									

PART XIV: CONCLUSIONS AND DISCUSSION

112. Since rubber can be manufactured in a variety of shapes, densities, etc., its use as a regulating membrane for the release of herbicides allows the evaluation of the phytozone intoxication concept.

113. Carbon black, as an additive, will retard loss rate. Such slowing of internal diffusion is probably proportional, to a limit, to the amount of black used and inversely proportional to the particle size. Both black and phenolic "microballoons" can be used as an artificial means of exceeding the solubility limit of BEE in natural rubber.

114. Natural rubber, because of its low cost, high biodegradation potential, and high solvency for BEE is the proper matrix choice.

115. The superior candidate formulations are listed in table C24.

Table C24

Superior Candidate Slow-Release Herbicides
(Ranked in Order of Efficacy)

Target	Formulations	% BEE	Release Rate mg/cm^2-day	Type	Longevity months
Water hyacinth	14ACE-A,B	22/18	0.03	Suspenders	21
	11ACE-E	22	-2	Sinkers	--
	18ACE-B	34	0.19	Sinkers	9
	18ACE-F	28	--	Sinkers	--
Elodea (potted)	11ACE-E	22	--	Sinkers	--
	17ACE-B	37	0.08	Sinkers	22
	15ACE-B(H)	38	0.07	Sinkers	27
Water milfoil (potted)	11ACE-E	22	--	Sinkers	--
	14ACE-A,B	22/18	0.03	Suspenders	21
	15ACE-B(2)	38	--	Sinkers	--
	17ACE-B	37	0.08	Sinkers	22
Alligator weed (potted)	11ACE-E	22	--	Sinkers	--

116. The inferiority of floating pellets is marked in the

laboratory. However, field conditions may be such as to allow mixing of the 2,4-D surface-film release with possible adequacy in the natural environment.

117. The first year's effort demonstrated that (a) the butoxyethanol ester of 2,4-D can be incorporated in simple, inexpensive, elastomeric matrices and will (b) release into a surrounding water environment via a diffusion dissolution mechanism, and will (c) destroy water hyacinth, water milfoil, and probably elodea.

118. During the second year the feasibility of manufacturing pellets and suspenders was shown, although costs were high. Future costs will, of course, depend upon demand. High demand will encourage full-scale manufacturing and prices of around $1.50 per pound.

119. Lifetimes in excess of 9 months have been estimated from loss rate analysis.

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APPENDIX D

DISSIPATION OF 2,4-D RESIDUES IN PONDS, LAKES, BAYOUS, AND OTHER QUIESCENT OR SLOWLY MOVING BODIES OF WATER

University of Southwestern Louisiana
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DISSIPATION OF 2,4-D RESIDUES IN PONDS, LAKES, BAYOUS, AND OTHER QUIESCENT OR SLOWLY MOVING BODIES OF WATER*

by

Edward O. Gangstad and William K. Averitt**

Abstract

This study was made to determine 2,4-D residues and their dissipation rates in surface water after treatment to control aquatic vegetation. Parameters found to affect residue levels are: rate of treatment for 1-, 4-, and 10-lb acid equivalent per surface acre; dilution in water for 1-, 3-, 5-, and 7-ft depths; mean temperature for April, May, July, September, November, and December treatments; and elapse time for 1, 7, 14, and 28 days after treatment. Partial correlation analyses indicated that all factors contributed to the rate of dissipation, and a partial regression equation was developed for prediction of residues after herbicide treatment. For the standard level of treatment, i.e. 4-lb acid equivalent per acre, the dissipation rates are: 58-ppb decrease in residue for each 2-ft increase in depth of water treated; 115-ppb decrease in residue for each 10 F increase in temperature above 60 F mean temperature; and 53-ppb decrease in residue for each 7-day interval of time after treatment.

Introduction

1. The U. S. Army Corps of Engineers has been actively engaged in the control and eradication of obnoxious plants since the first Congressional appropriation for that purpose in 1897. Water hyacinth

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* Research Contribution of the Office, Chief of Engineers, Washington, D. C., and the University of Southwestern Louisiana, Lafayette, La., under contract DACW-68-C-0006. Paper presented at the National Meetings of Weed Science Society of America, February 9-11, 1971, Dallas, Tex.

** Chief, Aquatic Plant Control, Office, Chief of Engineers, Washington, D. C., and Associate Professor, Department of Chemical Engineering, University of Southwestern Louisiana, respectively.

(*Eichhornia crassipes* (Mart) Solms) and alligater weed (*Alternanthera philoxeroids* (Mart) Grieb) have been the most serious plant problems in Louisiana and other states of the Atlantic and Gulf coasts. Mechanical methods were originally used for aquatic plant control, but these methods have been largely replaced by chemical and biological methods which are more economical and more effective. Because data on the rate of dissipation of 2,4-D residues in the aquatic environment are quite limited, the purpose of this study was to determine the amounts of 2,4-D residue in surface water after treatment to control aquatic vegetation and the time required for these residues to be dissipated.

Parameters affecting residue levels

2. The concentration of detectable amounts of the herbicide 2,4-D in surface water is known to be determined by such abiotic (nonliving) factors as the rate of treatment and the extent of dilution as affected by depth, flow, or addition of water to the system. Photodegradation[1] and absorption of the hydrosoil[2] are not found to be major routes for reduction of 2,4-D residues, but biodegradation by microorganisms[3] and metabolism by plants[4] are found to be major routes of herbicide decomposition. Temperature and time are important parameters affecting the rate of dissipation because they are known to influence biological processes to a large degree.

Ecological effects of herbicide treatment

3. Direct effects of repeated use of herbicides such as 2,4-D on the aquatic environment are relatively minor if the herbicides are used properly. Indirect effects may conceivably result in particular changes in the environmental system over a period of time. These changes, however, are not necessarily detrimental, for single organisms are not indispensible to an ecological community and many different organisms compete for the same niche. The most obvious ecological effect of herbicide application is the reduction of the plant population to an earlier point in the succession. This again is not a serious or lasting problem because many different organisms are known to be able

weed around the outside perimeter which was made available for testing in September 1966. Chemical control at this location had not been previously attempted. The dimethylamine salt of 2,4-D was applied by boat as a coarse spray at the rate of 4 lb ae/A for plots approximately one-hundredth of an acre in size. Samples were taken at regular intervals within each plot, and analyzed for 2,4-D.

11. Additional field studies on the residues of 2,4-D in surface water were initiated at Spanish Lake, New Iberia, La., in May 1968. Two test sites were selected in a small canal which was closed at one end and was adjacent to the lake. Test plots were 50 by 40 ft in area in a solid mat of alligator weed. The water depth was approximately 5 ft. Plots were treated in the usual manner at a rate of 1 and 10 lb ae/A on 23 May and 29 June. Within each test plot, four areas were sampled about 6 in. below the surface. The data are reported at the level of treatment and computed at a level of 4 lb ae/A for comparison with other treatments.

Results and Discussion

12. Laboratory and field data are summarized in tables D1 and D2, respectively, for test site, month of treatment, rate of treatment, long-range temperature, and residue levels of 2,4-D in parts per billion for 1, 7, 14, and 28 days after treatment. Substantial differences for particular conditions are observed within each study.

Laboratory tests

13. Results of plastic pool tests for 2,4-D dimethylamine and the propylene glycol butyl ester for November and May treatments indicate the relative differences due to formulation and month of application. At 28 days after treatment, residues of 275 and 527 ppb were observed for November with an average temperature of 61 F as compared with 34 and 64 ppb in May with an average temperature of 75 F. The 2,4-D amine was dissipated more rapidly in both November and May treatments.

Table D1

Residues of 2,4-D (in parts per billion)

in Surface Water, Laboratory Tests

Test Site	Month Treated	Application Rate lb/A	Water Depth ft	Long-Range Mean Temp °F		Days After Treatment 1	7	14	28
Plastic pools*	Nov	4	1	61		356	492	582	259
	Nov	4	1	61		307	506	622	291
					Mean	331	499	602	275
Plastic pools**	Nov	4	1	61		450	407	753	432
	Nov	4	1	61		374	356	684	623
					Mean	412	381	717	527
Plastic pools*	May	4	1	75		739	50	31	11
	May	4	1	75		696	57	13	58
					Mean	717	53	22	34
Plastic pools**	May	4	1	75		789	72	56	40
	May	4	1	75		874	126	49	89
					Mean	831	89	52	64
Swimming pools†	May	4	3	75		52	264	168	32
	May	4	3	75		156	312	248	24
					Mean	104	288	203	28
Swimming pools†	July	4	3	82		43	240	148	53
	July	4	3	82		80	200	185	28
					Mean	61	220	166	41
Swimming pools†	May	1	3	75		13	66	42	16
	July	1	3	82		29	78	58	33
					Mean	21	72	50	25
Swimming pools†	May	10	3	75		108	518	371	133
	July	10	3	82		199	504	433	107
					Mean	154	511	402	120
		Least significant difference P = 05				175	30	39	60
		Least significant difference P = 01				247	43	55	85

* Outdoor pools, covered to keep out rainfall, 4 ft by 2 ft by 1 ft, Lafayette, La., treated with 2,4-D amine salt.

** Outdoor pools, covered to keep out rainfall, 4 ft by 2 ft by 1 ft, Lafayette, La., treated with 2,4-D ester.

† Outdoor pools, not covered to keep out rainfall but adjusted to a constant level, New Iberia, La., treated with 2,4-D amine salt.

weed around the outside perimeter which was made available for testing in September 1966. Chemical control at this location had not been previously attempted. The dimethylamine salt of 2,4-D was applied by boat as a coarse spray at the rate of 4 lb ae/A for plots approximately one-hundredth of an acre in size. Samples were taken at regular intervals within each plot, and analyzed for 2,4-D.

11. Additional field studies on the residues of 2,4-D in surface water were initiated at Spanish Lake, New Iberia, La., in May 1968. Two test sites were selected in a small canal which was closed at one end and was adjacent to the lake. Test plots were 50 by 40 ft in area in a solid mat of alligator weed. The water depth was approximately 5 ft. Plots were treated in the usual manner at a rate of 1 and 10 lb ae/A on 23 May and 29 June. Within each test plot, four areas were sampled about 6 in. below the surface. The data are reported at the level of treatment and computed at a level of 4 lb ae/A for comparison with other treatments.

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12. Laboratory and field data are summarized in tables D1 and D2, respectively, for test site, month of treatment, rate of treatment, long-range temperature, and residue levels of 2,4-D in parts per billion for 1, 7, 14, and 28 days after treatment. Substantial differences for particular conditions are observed within each study.

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13. Results of plastic pool tests for 2,4-D dimethylamine and the propylene glycol butyl ester for November and May treatments indicate the relative differences due to formulation and month of application. At 28 days after treatment, residues of 275 and 527 ppb were observed for November with an average temperature of 61 F as compared with 34 and 64 ppb in May with an average temperature of 75 F. The 2,4-D amine was dissipated more rapidly in both November and May treatments.

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	May	4	1	75	874	126	49	89
				Mean	831	89	52	64
Swimming pools†	May	4	3	75	52	264	168	32
	May	4	3	75	156	312	248	24
				Mean	104	288	203	28
Swimming pools†	July	4	3	82	43	240	148	53
	July	4	3	82	80	200	185	28
				Mean	61	220	166	41
Swimming pools†	May	1	3	75	13	66	42	16
	July	1	3	82	29	78	58	33
				Mean	21	72	50	25
Swimming pools†	May	10	3	75	108	519	371	133
	July	10	3	82	199	504	433	107
				Mean	154	511	402	120
Least significant difference P = 05					175	30	39	60
Least significant difference P = 01					247	43	55	85

* Outdoor pools, covered to keep out rainfall, 4 ft by 2 ft by 1 ft, Lafayette, La., treated with 2,4-D amine salt.

** Outdoor pools, covered to keep out rainfall, 4 ft by 2 ft by 1 ft, Lafayette, La., treated with 2,4-D ester.

† Outdoor pools, not covered to keep out rainfall but adjusted to a constant level, New Iberia, La., treated with 2,4-D amine salt.

Table D2

Residues of 2,4-D (in parts per billion)

in Surface Water, Field Tests

Test Site	Month Treated	Application Rate lb/A	Water Depth ft	Long-Range Mean Temp °F	Days After Treatment 1	7	14	28
Mouton	Sep	4	3	72	556	57	20	9
Pond*	Sep	4	3	72	[illegible]	27	[illegible]	9
				Mean	[illegible]	[illegible]	[illegible]	[illegible]
Bayou	Dec	4	7	57	37	727	37	1
Teche**	Dec	4	7	57	30	900	85	1
				Mean	33	813	61	1
Rogers	Apr	4	3	62	275	215	97	[illegible]
Pond†	Apr	4	3	63	221	276	145	45
				Mean	248	245	121	24
Park	May	4	7	79	695	55	40	[illegible]
Lagoon††	May	4	7	79	967	[illegible]	[illegible]	19
				Mean	831	66	[illegible]	19
Spanish	May	4	5	75	32	104	132	[illegible]
Lake‡	May	4	5	75	29	[illegible]	104	[illegible]
				Mean	[illegible]	[illegible]	118	[illegible]
Spanish	Jul	4	5	82	52	[illegible]	32	1
Lake‡	Jul	4	5	82	60	39	42	[illegible]
				Mean	56	111	37	[illegible]
Spanish	May	1	5	75	5	51	55	[illegible]
Lake‡	Jul	1	5	82	18	[illegible]	[illegible]	25
				Mean	12	[illegible]	[illegible]	[illegible]
Spanish	May	1	5	75	71	[illegible]	[illegible]	[illegible]
Lake‡	Jul	1	5	82	131	[illegible]	[illegible]	7
				Mean	[illegible]	[illegible]	[illegible]	[illegible]
		Least significant difference P = .05			[illegible]	104	[illegible]	14
		Least significant difference P = .01			211	140	[illegible]	20

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* Small pond approximately [illegible] acre in size and 3 ft deep near Lafayette, La., treated with 2,4-D amine salt.

** Houseboat slip, 50 ft wide, 7 ft deep, near St. Martinville, La., treated with 2,4-D amine salt.

† Small pond about 1 acre in size and 3 ft deep, near Lafayette, La., treated with 2,4-D amine salt.

†† Small lagoons about 1[illegible]0 ft wide and 7 ft deep in New Orleans City Park. 2,4-D amine introduced into the propeller wash.

‡ Small lake with test plots located in an adjacent canal near New Iberia, La., 5 ft deep. Treated with 2,4-D amine salt.

Results of swimming pool tests at 4 lb ae/A at the 28th day did not differ significantly from plastic pool tests, but are substantially lower for the first dates of sampling.

Field tests

14. Results of field studies as listed in table D2 for residues of 2,4-D show the same general trend to decrease with time as days after application, and were reduced to about 100 ppb, 14 days after treatment when applied at a level of 4 lb ae/A. At the initial stages after treatment, relatively large differences in residue were observed, related to test site. Residues in Mouten Pond, Rogers Pond, and the Park Lagoons were relatively high on the first date of sampling but tended to decrease rapidly thereafter. Residues at Bayou Teche and Spanish Lake were low during the first date of sampling, tended to increase up to the 7th day after treatment and decreased rapidly after this point. It is assumed that these discrepancies are due to absorption on the vegetation and hydrosoil and later released to the surface water. Water hyacinths treated in December in Bayou Teche were killed completely by the tenth week after treatment as compared with the fourth week after treatment in Rogers Pond, treated in April. It is assumed that this difference in rate of activity is due to temperature. Differences in the residue level are apparent for depth of water and rates of application in the City Park Lagoons and in Spanish Lake treatments.

Partial correlation analysis

15. The parameters observed in tables D1 and D2 are the most obvious effects related to field application; that is, the rate in pounds acid equivalent per acre, depth of the water treated, mean temperature of the aquatic environment, and time lapse in days after treatment. However, direct inspection of the data does not lead to definite conclusions as to which of these functions has the greatest effect on the dissipation of 2,4-D residues, nor to which conditions are most critical for rapid dissipation.

16. For further evaluation, the data were processed for partial

correlation analysis and the results are summarized in table D3 for the input summary and the correlation matrix. The input summary shows that most of the variability is in parts per billion residue of 2,4-D. The standard deviation and the coefficients of variation in percent of the mean are also greatest in parts per billion 2,4-D. It is assumed that a number of unmeasured factors contribute to this variability.

Table D3

Input Summary and Correlation Matrix of Partial Correlation Analysis of Rate, Depth, Temperature, Time, and Residue

Input Summary

Variable		Mean	Variance	Std Dev	CV% M
Rate, lb/surface area	X1	4.375000	5.518868	2.349227	53
Depth, ft	X2	3.475000	3.798113	1.948875	55
Temp, F	X3	73.687500	59.713050	7.727422	14
Time, days after treatment	X4	14.243750	92.81046	9.634024	68
Residue, ppb 2,4-D	X5	177.356250	50729.513793	225.232133	128

Correlation Matrix

Rate, lb/surface area	X1	1.000000				
Depth, ft	X2	0.043272	1.000000			
Temp, F	X3	0.092763	0.091773	1.000000		
Time, days after treatment	X4	-0.000729	0.003894	-0.002772	1.000000	
Residue, ppb 2,4-D	X5	0.159427	-0.278733	-0.396324	-0.325054	1.000000

17. The correlation matrix shows a positive relation between the rate of application and the residue level and negative relations to

other variables. Thus, the increase in the rate of treatment increases the residue concentration, the increase in depth reduces the residue concentration, the increase in temperature reduces the residue concentration, and the increase in time after treatment reduces residue concentration. These relations conform to generally observed rates of herbicide action in field operation.

Multiple regression equation

18. For further study of these different functions, the multiple correlation coefficients were calculated, using the TYMSHARE STEPREG-1 program, holding each variable constant with forced exclusion of each variable. The index of dependent variable X_5 (ppb residue) and analysis of variance are given in table D4. The highest multiple index of determination was obtained with X_5 as the dependent variable, including all variables measured. The partial correlation is highly significant ($r^2 = 0.3643$; $R = 0.60$), accounting for 36 percent of the total variation. The greatest slope is obtained for X_2 (depth) and the least for X_4 (time). The multiple regression equation is: $X_5 = 1144.4644 - 11.466X_3 - 7.5989X_4 - 28.9349X_2 + 19.7998X_1$.

Practical application

19. The dissipation of 2,4-D residues as stated above depends upon a number of partially dependent variables, namely, rate of application, dilution, temperature, time after application, etc. While it is desirable to determine these factors individually for scientific evaluation, from a practical point of view it is sufficient to know the combined rate at which these changes take place and the level at which they have a negligible effect. Table D5 has been prepared to give the predicted values likely to be encountered in field practice. From the generalized equation as discussed above, we observe for the standard level of treatment, i.e., 4 lb ae/A, the dissipation rates are: 58 ppb decrease in residue for each 2-ft interval increase in depth of water treated; 115 ppb decrease in residue for each 10 F increase in temperature above 60 F mean temperature; and 53 ppb decrease in residue for each 7-day

Table D4

Index of Dependent Variable 5 and Analysis of Variance

Index of Dependent Variable 5

Step 1 variable 3 added, index = 0.157073
Step 2 variable 4 added, index = 0.263449
Step 3 variable 2 added, index = 0.322061
Step 4 variable 1 added, index = 0.364291

Multiple index of determination = 0.364291
F ratio 4.155:22.2056*

Analysis of Variance

Variable	Coefficient	Variance	T-Test	Beta
Constant	1144.4644	19,956.3180	8.1014*	
3	-11.4666	3.5422	-6.0926*	-334.2193
4	-7.5989	2.2417	-5.0752*	-177.6524
2	-28.9349	55.3139	-3.8905**	-3344.0151
1	19.7998	38.0737	3.2088**	1898.3049

* Highly significant, P = 01.
** Significant, P = 05.

interval of time after treatment. Because of the generalized nature of this study, the predicted values are likely to apply to most areas of the Atlantic and Gulf coast.

Table D5

Predicted Residue Levels (in parts per billion)

Application Rate lb/acre	Depth ft	Temp, °F	Days After Treatment			
			1	7	14	28
2	3	60	402	356	303	196
		70	287	241	188	81
		80	172	126	72	--
	5	60	344	298	245	139
		70	229	182	130	24
		80	114	68	16	--
	7	60	286	240	187	81
		70	171	125	72	--
		80	57	11	--	--
4	3	60	442	396	342	236
		70	327	281	228	121
		80	212	166	113	7
	5	60	384	337	284	178
		70	269	223	170	64
		80	154	108	55	--
	7	60	326	279	227	120
		70	210	165	112	6
		80	96	51	--	--
8	3	60	520	474	421	315
		70	405	360	307	200
		80	291	246	192	86
	5	60	463	417	364	257
		70	348	302	249	143
		80	233	187	134	28
	7	60	405	359	306	199
		70	290	244	191	84
		80	175	128	76	--

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